Published Monthly. Price, $5.00 per Annum.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

VOL. XIX.—NO. 11.

NOVEMBER, 1897.

EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE,
COMMITTEE ON PAPERS AND PUBLICATIONS.

CONTENTS.

PAGE.

Proceedings ..... (57)-(62)

PAPERS.

The Solubility of Stannous Iodide in Water and in Solutions of Hydriodic Acid. By S. W. Young 845
On Iodostannous Acid. By S. W. Young 851
A Comparison of Various Rapid Methods for Determining Carbon Dioxide and Carbon Monoxide. By L. M. Dennis and C. G. Edgar 859
The Electrolytic Determination of Cadmium. By Daniel L. Wallace and Edgar F. Smith 870
On the Reactions between Mercury and Concentrated Sulphuric Acid. By Charles Baskerville and F. W. Miller 873
On the Determination of Fat and Casein in Feces. By Herman Poole 877
The Principal Amid of Sugar-Cane. By Edmund C. Shorey 881
The Influence of Antiseptics on the Digestion of Blood Fibrin by Pepsin in a Hydrochloric Acid Solution. By Charles F. Mabery and Leo Goldsmith 889
Review: Some Records of Recent Progress in Industrial Chemistry. 894
Obituary 918
Books Received 921

REVIEW OF AMERICAN CHEMICAL RESEARCH 151-164

EASTON, PA.:
CHEMICAL PUBLISHING COMPANY.

Entered at the Post Office, Easton, Pa., as Second Class Matter.

Orders for back numbers of the Journal should be addressed to the Librarian, F. E. Dodge, 316 Bowne Ave., Flushing, N. Y.

OFFICERS OF THE AMERICAN CHEMICAL SOCIETY.

President: Charles B. Dudley, Drawer 334, Altoona, Pa.

Vice-Presidents: The Presiding Officers of the Local Sections; see below.

General Secretary: Albert C. Hale, 551 Putnam Ave., Brooklyn, N. Y.

Treasurer: C. F. McKenna, 221 Pearl st., N. Y. City.

Librarian: F. E. Dodge, 316 Bowne Ave., Flushing, N. Y.

Committee on Papers and Publications: Edward Hart, Editor; J. H. Long; Thomas B. Osborne.

Committee on Nominations to Membership: A. A. Breneman; P. T. Austen; C. A. Doremus.

Finance Committee: Durand Woodman; A. P. Hallock; A. H. Sabin.

Board of Directors. Members ex-officio: Charles B. Dudley, Pres.; Albert C. Hale, Gen. Sec.; C. F. McKenna, Treas.; F. E. Dodge, Librarian; Edward Hart, Editor. *Term expires Dec. 1897:* Charles F. Chandler; Peter T. Austen; Charles E. Munroe; Albert B. Prescott. *Term expires Dec. 1898:* H. W. Wiley; Wm. McMurtrie; C. A. Doremus; A. A. Breneman.

Council. Members ex-officio: Charles B. Dudley, Pres.; Albert C. Hale, Gen. Sec.; Edward Hart, Editor. *Term expires Dec. 1897:* G. F. Barker; F. W. Clarke; W. L. Dudley; A. A. Noyes. *Term expires Dec. 1898:* J. W. Mallet; Albert B. Prescott; Thomas H. Norton; G. C. Caldwell. *Term expires Dec. 1899:* C. F. Chandler; C. E. Munroe; Wm. McMurtrie; W. A. Noyes.

Local Sections. Rhode Island Section: Edward D. Pearce, Pres. Officer; Walter E. Smith, Sec., 47 Jenkins St., Providence, R. I. *Cincinnati Section:* W. L. Dudley, Pres. Officer; S. Waldbott, Sec., Lloyd Library, 224 W. Court St., Cincinnati, O. *New York Section:* Wm. McMurtrie, Pres. Officer; Durand Woodman, Sec., 127 Pearl St., N. Y. City. *Washington Section:* W. D. Bigelow, Pres. Officer; V. K. Chesnut, Sec., U. S. Dept. of Agr. *Lehigh Valley Section:* Jos. W. Richards, Pres. Officer; Bernard Enright, Sec., 330 E. 4th St., So. Bethlehem, Pa. *New Orleans Section:* A. L. Metz, Pres. Officer; Hubert Edson, Sec., Bartels, La. *Nebraska Section:* H. H. Nicholson, Pres. Officer; John White, Sec., Box 675, Lincoln, Neb. *Chicago Section:* Wm. Hoskins, Pres. Officer; F. B. Dains, Sec., 2421 Dearborn st., Chicago, Ill. *North Carolina Section:* F. P. Venable, Pres. Officer; W. A. Withers, Sec., A. and M. College, Raleigh, N. C.

PAPERS ACCEPTED FOR PUBLICATION:

The Rate of Solution of Solid Substances in Their Own Solutions. By Arthur A. Noyes and Willis R. Whitney.

The Analysis of Bearing-Metal Alloys. By W. E. Garrigues.

Obituary of Dr. Meinhard Alsberg. By H. Endemann.

VOL. XIX. [NOVEMBER, 1897.] NO. 11.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE SOLUBILITY OF STANNOUS IODIDE IN WATER AND IN SOLUTIONS OF HYDRIODIC ACID.

BY S. W. YOUNG.

Received July 31, 1897.

THE following experiments have been made in order to determine the solubility of stannous iodide in water and in different strengths of hydriodic acid at different temperatures.

The stannous iodide used was prepared by the action of hydriodic acid on tin. The hot saturated solutions thus obtained were cooled and the separated crystals of stannous iodide were filtered off by suction, dried on bibulous paper for a few minutes, and then transferred to a large test-tube and shaken repeatedly with carbon bisulphide in order to dissolve out the stannic iodide which is always present. The product was kept under carbon bisulphide in tightly stoppered tubes until wanted.

The hydriodic acid used was prepared by the action of hydrogen sulphide on iodine and water. It was found convenient in preparing an acid of given strength to weigh out the requisite amounts of water and iodine and allow the hydrogen sulphide to act on them. It is possible in this way to prepare acids of any strength with very considerable accuracy. For instance, in one case it was desired to make an acid of thirty per cent. After the acid was prepared analyses gave 29.93 per cent. and 29.97 per cent.

The method used in determining the solubility was as follows:

The requisite solvent and stannous iodide were placed in a large 100 cc. test-tube, which was closed by a stopper with three holes, one for a thermometer reading to tenths, one for a stirrer, and one for the introduction of a pipette for removing the samples. A layer of coal oil about one inch deep was placed upon the solution to prevent oxidation. The whole was heated nearly to boiling for a few moments and stirred constantly to insure saturation. The whole was then supported in a large beaker of boiling water. When the thermometer had remained constant for some time a weighing pipette was introduced and a sample withdrawn, weighed, and the amount of stannous salt determined by titration with standard iodine solution, according to the method described in a previous paper.[1]

In withdrawing the sample in the pipette it was necessary that the solution should be filtered to avoid drawing out more or less solid stannous iodide. This was accomplished by affixing to the tip of the pipette a short piece of rubber tubing, in which was placed a wad of absorbent cotton. The solution, after passing through this filter, was perfectly clear.

Following are the results of two series of determinations of the solubility of stannous iodide in pure water:

Series 1.		Series 2.	
T.	P.	T.	P.
98.5	3.43	97.3	3.70
84.9	3.05	87.4	3.24
73.9	2.56	77.6	2.75
60.1	2.09	67.5	2.34
51.5	1.79	59.7	2.03
41.0	1.50	49.5	1.72
30.5	1.21	39.4	1.38
20.8	1.03	29.6	1.11
		19.8	0.96

T = Temperature.
P = Parts stannous iodide in 100 of solution.

The two series show very good agreement with the exception of the first numbers, the second series having a value of 3.70 parts soluble at 97.3°, while the first series shows only 3.43 parts at 98.5°. This is undoubtedly due to incomplete saturation in the first series. This is indicated by the fact that the curves plotted from the data are more nearly normal with the higher value. The same thing was noticed in some other series.

[1] This Journal, 19, 809.

In Table I, following, are the results of eight series of determinations of the solubility of stannous iodide, in solutions of hydriodic acid, varying in strength from five to thirty-seven per cent. Some of the numbers are averages of duplicates, while some are single determinations. A few experiments showed the method of determination to be very reliable and it seemed probable that the error introduced by oxidation on standing sufficiently long for two parallel determinations to be made, would be greater than any error introduced by the method.

Two peculiarities are immediately noticeable from a study of these data. The first one is that the presence of hydriodic acid up to above fifteen per cent. renders the stannous iodide less soluble than in pure water. In order to show more clearly the nature of this effect the following series of experiments was made:

Solutions of hydriodic acid varying from three to fifteen per cent. were prepared by taking strong acid of known strength and diluting with the calculated amounts of water. These were saturated with stannous iodide by warming and allowed to cool to 23.5° C., at which temperature they were allowed to stand for some time with frequent stirring, in order to insure equilibrium. Portions were taken out from each in a weighing pipette and titrated. Following are the results. They cannot lay claim to extreme accuracy, owing to the rather large probable error introduced by the method of making up the dilute acids used:

Strength of acid. Per cent.	P.[1]	Strength of acid. Per cent.	P.
0	1.00	9	0.21
3	0.26	10	0.26
4	0.22	11	0.30
5	0.19	12	0.45
6	0.16	13	0.58
7	0.16	14	0.62
8	0.17	15	0.81

P = Parts of stannous iodide in one hundred of solution.

These results show that the solubility of stannous iodide decreases with the increase in concentration of the hydriodic acid up to between six and seven per cent., and thereafter increases. The decrease in solubility reminds one of the conduct of common salt and hydrochloric acid. The later increas-

TABLE I.

Showing Solubility of Stannous Iodide in Solutions of Hydriodic Acid of Different Concentrations.

Strength of hydriodic acid used =	5.83 per cent.		9.50 per cent.		10.60 per cent.		15.20 per cent.		20.44 per cent.		24.80 per cent.		30.40 per cent.		36.82 per cent.	
	T.[1]	P.[2]	T.	P.	T.	P.	T.	P.	T.	P.	T.	P.	T.	P.	T.	P.
	98.2	2.06	89.5	1.39	98.1	2.11	95.0	2.68	98.7	5.44	99.4	8.15	89.7	13.35	97.6	24.80
	80.6	1.23	79.8	1.12	84.3	1.38	83.3	1.96	81.0	3.65	89.5	7.23	79.6	11.65	85.0	22.12
	70.6	0.90	69.7	0.83	69.0	0.87	70.9	1.44	69.0	2.88	79.4	5.96	69.9	10.70	73.3	20.66
	57.9	0.63	59.5	0.57	59.4	0.64	60.4	1.03	59.5	2.46	68.4	5.07	59.3	9.87	59.2	19.74
	49.8	0.39	50.0	0.40	49.8	0.45	50.0	0.84	49.5	2.15	59.8	4.54	49.3	9.44	49.5	19.32
	41.1	0.37	40.0	0.29	40.2	0.33	40.3	0.77	40.1	1.87	50.0	4.16	39.1	9.05	40.0	18.80
	30.3	0.23	29.8	0.23	30.0	0.23	30.0	0.67	30.9	1.80	39.7	3.96	31.0	9.52	30.0	18.88
	23.3	0.16	18.3	0.21	20.3	0.20	17.6	0.56	17.7	1.75	30.0	3.86	18.7	9.87	21.0	20.10
	..	..	..	..	..	..	..	..	..	..	20.0	4.06	..	..	..	..
	..	..	..	..	..	..	..	..	..	..	14.5	4.20	..	..	..	..
	..	..	..	..	..	.	..	..	..	..	4.5	4.94	..	..	..	..

[1] T = Temperature.

[2] P = Parts stannous iodide in one hundred of solution.

ing solubility would seem to indicate the introduction of a new system in about seven per cent. concentration of hydriodic acid. The nature of this new system will be discussed later.

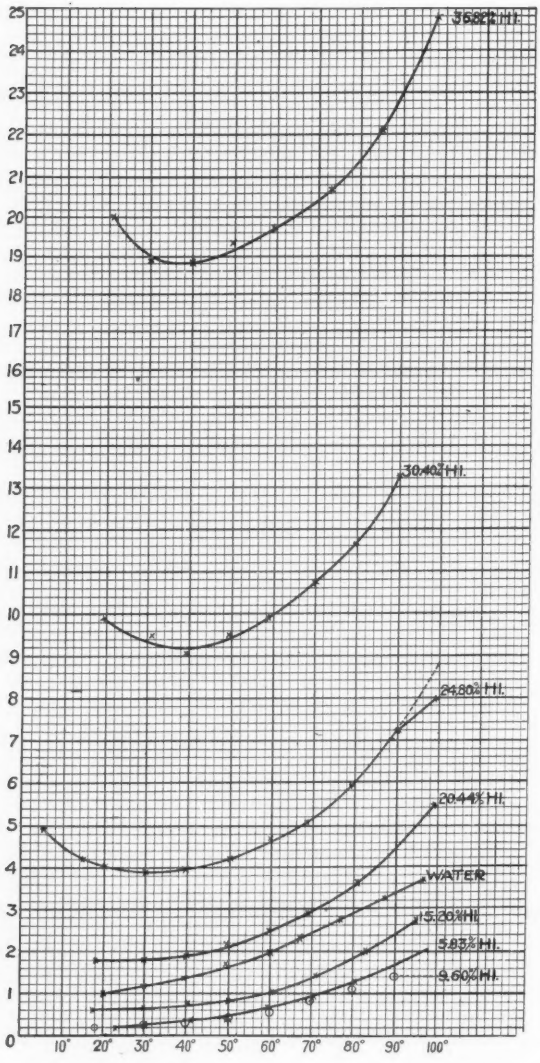
The second notable peculiarity in the result is that in concentrations of hydriodic acid, from twenty-five per cent. up, there is a very notable *increase* in the solubility with *decreasing* temperature from somewhere between 30° and 40°. This is most strikingly shown by the accompanying curves.

An inspection of these curves will readily show that there are distinct differences in their characters apart from the merely general increase or decrease in solubility occasioned by the different strengths of acid.

Comparing all curves for solubility in acid with that for solubility in water, it will be seen that the former all differ distinctly from the latter in two particulars. In the first place, above about 40° to 50° the solubility in acids increases more rapidly than does that in water, *i. e.*, the curves above this temperature are steeper for acids than for water. Below this temperature, however, the reverse is true, the curves being less steep for acids than for water, except that with acids of above twenty per cent. the pitch of the curve changes entirely between 30° and 40° and the solubility increases with decreasing temperature.

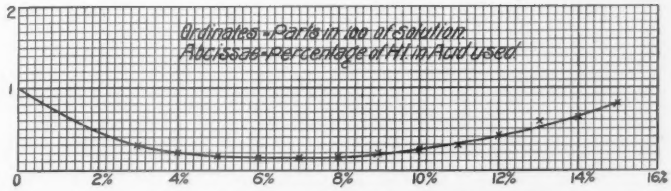
This abnormality would seem to indicate the introduction of a new system at lower temperatures, which, perhaps, becomes more and more stable with falling temperature, and by its greater solubility produces the peculiar character shown in the curves below 40°. The nature of this new system has been determined and will be made the subject of the following paper.

For convenience of reference the following table has been prepared. It contains the values for the solubilities of stannous iodide in water and hydriodic acid for temperatures from 20° to 100°. The values are taken from the points of intersection of the curves, and are expressed in parts per hundred of solvent instead of parts per hundred of solution as previously.



Curves showing solubility of stannous iodide at different temperatures in hydriodic acids of different strengths.

Ordinates = Parts stannous iodide in 100 of solution. Abscissae = Temperatures.



Curve showing solubility of stannous iodide in hydriodic acids of different strengths at 23.5° C.

TABLE II.

SHOWING THE VALUES FOR THE SOLUBILITY OF STANNOUS IODIDE IN VARIOUS CONCENTRATIONS OF HYDRIODIC ACID. VALUES TAKEN FROM INTERSECTIONS OF CURVES AND CALCULATED TO PARTS IN 100 OF SOLVENT.

Per cent. strength of HI =	Water.	5.83	9.60	15.20	20.44	24.80	30.40	36.82
Temperature.								
20°	0.98	0.20	0.23	0.60	1.81	4.20	10.86	25.31
30°	1.16	0.23	0.23	0.64	1.81	4.06	10.28	23.46
40°	1.40	0.33	0.28	0.71	1.90	4.12	10.06	23.15
50°	1.69	0.46	0.38	0.82	2.12	4.34	10.35	23.76
60°	2.07	0.66	0.55	1.11	2.51	4.78	11.03.	24.64
70°	2.48	0.91	0.81	1.37	2.92	5.43	11.97	25.72
80°	2.95	1.23	1.13	1.83	3.70	6.38	13.30	27.23
90°	3.46	1.65	1.52	2.40	4.58	7.82	15.52	29.84
100°	4.03	2.23	2.04	3.63	5.82	9.60	....	34.05

STANFORD UNIVERSITY,
July 17, 1897.

ON IODOSTANNOUS ACID.

BY S. W. YOUNG.

Received July 31, 1897.

AS has been pointed out in the previous paper, the solubility of stannous iodide in rather strong solutions of hydriodic acid, indicates the formation at low temperatures of a system of different character from that existing at higher temperatures.

In order to become more familiar with the facts of the case, the following experimental work was performed.

In the first place it was noticed that when saturated solutions of stannous iodide in hydriodic acid of about twenty-five per cent. or over, were cooled in ice-water, very light yellow needles crystallized out in greater or less quantity, and it was evident that these were entirely different in character from the red needles of stannous iodide itself.

Several unsuccessful attempts to dry samples of the product for analysis were made. In the first instance the product was filtered off by suction and transferred to a vacuum desiccator. It almost immediately began to turn red. A sample was next placed in a current of dry hydrogen, but this suffered the same discoloration as the first. It was next attempted to dry a sample in a current of dry hydrogen, the vessel containing the sample, as also the hydrogen, being kept at 0° C. by ice-water. Again the substance became red, but more slowly than in the previous experiments.

The most natural inference from these preliminary experiments was that the compound was iodostannous acid, H_2SnI_4, or $SnI_2.2HI$, analogous to chlorostannous acid, H_2SnCl_4. It was thought that if this were the case it might be possible to dry the compound at low temperatures in an atmosphere of gaseous hydriodic acid. Accordingly a sample was placed in a weighing bottle, which in turn was placed in a wide-mouthed glass-stoppered bottle, which also contained pieces of glacial phosphoric acid. A current of dry hydriodic acid gas was then conducted into the bottle to displace the air, the bottle immediately stoppered tightly and immersed in ice-water. After a few hours, however, this sample too had begun to redden, and the attempt to obtain the composition of the body by direct analysis was abandoned.

In the meantime experiments were carried on to study more closely the solubility of the bodies at lower temperatures.

The method was to take hydriodic acid of known strength, add to it stannous iodide more than sufficient to saturate the solution, cool in ice-water and determine the amount of stannous iodide in the solution by titration with standard iodine solution by the process described in the previous paper. Following are the data obtained, all results being given in terms of stannous iodide :

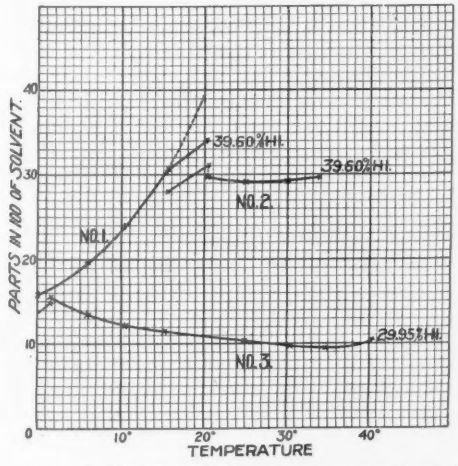
SOLUBILITY OF STANNOUS IODIDE AT LOW TEMPERATURES IN 39.6 PER CENT. HYDRIODIC ACID.

Temperature.	Parts in 100 of solution. I.	II.	Parts in 100 of solvent.
0°	13.52	13.56	15.66
5.7°	16.44	16.37	19.71
10.5°	19.47	19.60	24.27
15.7°	23.56	23.68	30.92
20.3°	25.50	25.60	34.30

The solution gave out at this point and another one was prepared in the same way with the same acid. Readings in this case were begun at 15.5°.

Temperature.	Parts in 100 of solution. I.	II.	Parts in 100 of solvent.
15.5	22.00	22.11	28.20
20.2	23.49	23.59	30.77
20.1	22.93	23.02	29.86
25.3	21.98	....	28.20
30.0	21.97	....	28.18
34.7	22.49	....	29.10

After making the reading at 20.2° the solution was allowed to stand for some hours, at the end of which time the solid in the solution which at the time of the first reading had been of the light-yellow sort, had changed completely into red stannous iodide. The yellow compound was thus stable under the conditions of the experiment up to about 20°. By reference to the accompanying curves it will be seen that in the preceding set of



Curves showing the solubility of iodostannous acid and of stannous iodide at low temperatures. All parts soluble in terms of stannous iodide.

experiments also, the solubility diverges from the normal between 15° and 20°. It will also be noticed that in the present series of determinations the solubility falls from 20° to 30°, and

thereafter rises. This may perhaps be taken to indicate that the system represented by the yellow compound is more or less stable in solution after it has ceased to be stable in the solid form in contact with solution.

One other series of solubility determinations was made, using acid of 29.95 per cent. Following are the results of this series :

Temperature.	Parts in 100 of solution.	Parts in 100 of solvent.
1.5°	12.96	14.89
1.5°	13.15	15.14
6.0°	12.35	14.09
10.5°	11.01	12.36
15.2°	10.48	11.70
24.8°	9.36	10.33
30.7°	8.78	9.62
34.8°	8.70	9.50
40.3°	9.51	10.50

Between the two readings at 1.5° the same transition of the yellow solid into the red that was spoken of above as occurring at 20° had taken place. As is noticed it was not accompanied by any marked change in solubility as was the case above. It is also to be noticed that what change there is is toward increase, while in the previous case it was toward decrease. The probable explanation of this will be made later.

DETERMINATION OF THE COMPOSITION OF THE YELLOW COMPOUND.

It was shown above that the determination of the composition of the yellow compound by direct analysis appeared to be impossible. The composition of the body has, however, been determined by the following method :

If a solution of hydriodic acid of known strength be saturated, or nearly so, with stannous iodide at ordinary temperatures, and the amount of stannous iodide contained in the solution be then determined, it is evident that we may very easily calculate the amounts of stannous iodide and hydriodic acid contained in one hundred parts of water.

If now this same solution be cooled to, say zero, and the yellow compound be allowed to crystallize out, it is evidently possible by analyses of the mother-liquor to determine the percentages of hydriodic acid and stannous iodide remaining, and from

this to calculate the parts of stannous iodide and of hydriodic acid remaining in one hundred parts of water. Then, if the yellow body be a compound of stannous iodide with hydriodic acid, both the parts per hundred of water of stannous iodide and of hydriodic acid will be decreased, and the ratio of the decrease will be the same as the ratio in which the two constituents are combined in the yellow solid. Following are the data essential for the calculation.

1. Determination of the strength of the hydriodic acid, used by titration with standard alkali, gave:

I.	II.
35.91	35.96

2. After saturating the requisite amount of the above acid and filtering the solution through cotton-wool under oil, the percentage of stannous iodide was determined and found to be:

I.	II.
16.94	16.92

3. From these data it follows by simple calculation that the original solution was constituted as follows:

Water	100	parts.
Stannous iodide	31.94	"
Hydriodic acid	56.14	"

4. The solution was now cooled to 0° C. and allowed to stand for some time to insure equilibrium. Very considerable quantities of the yellow body separated out.

5. The percentage of stannous iodide was determined by the usual method and found to be:

I.	II.	Average.
12.66	12.84	12.70

6. Since titrations with alkali cannot be made in presence of tin salts, the determination of the free hydriodic acid in the solution was found by taking weighed samples, diluting to 100 cc., and taking aliquot parts, and therein determining the total iodine by distilling off the iodine with ferric chloride in the Bunsen apparatus. Knowing the amount of stannous iodide in the solution already, the corresponding amount of iodine can be calculated. Subtracting this from the total iodine found, the remainder is the amount of iodine present as hydriodic acid. The follow-

ing determinations of total iodine in separately weighed samples were obtained :

I.	II.
38.73	38.55

Since the percentage of stannous iodide in this solution was found to be 12.70, it follows that the percentage of iodine in combination with tin is 8.71. Subtracting this from 38.60 (total iodine) gives 29.9 per cent. of iodine as hydriodic acid. This is equivalent to 30.14 per cent. hydriodic acid. Calculated to the basis of one hundred of water we get for the composition of the solution after crystallization :

Water	100	parts.
Stannous iodide	22.22	"
Hydriodic acid	52.72	"

These results show one hundred parts of water to have lost by crystallization 9.72 parts of stannous iodide and 3.42 parts of hydriodic acid, and these must be in combination in the yellow compound. A simple calculation shows this result to accord very closely with the formula $SnI_2.HI$, for

$$\text{Mol. wt. } SnI_2 : \text{Mol. wt. HI} :: \text{Amt. } SnI_2 : x$$
$$370.43 : 127.54 :: 9.72 : x$$
$$x = 3.35.$$

Theoretically then, in the compound $HSnI_3$ or $SnI_2.HI$, the amount of hydriodic acid in combination with 9.72 parts of stannous iodide would be 3.35. The value found was 3.42, which, considering the complexity of the process, should be considered very fair agreement.

The fact that the compound contains only one molecule of hydriodic acid instead of two, as was at first thought possible, is not particularly surprising, since it appears to be generally true that those double halides of stannous chloride which contain only one molecule of the alkali chloride are the most stable.

EXPLANATION OF SOME OF THE PECULIARITIES NOTICED IN THE SOLUBILITY CURVES OF STANNOUS IODIDE AT LOW TEMPERATURES.

Certain peculiarities in the solubility curves accompanying are noticeable, and some of them have been pointed out. The sudden breaks in the curves are particularly noticeable. The fact that this

break is not seen in curve No. 1, is undoubtedly due to the fact that the observations were not carried far enough, the solution having given out at 20°. Breaks are noticed in curve No. 2, at 20.2°, and in curve No. 3, at 1.5°. Since these breaks indicate the points at which rapid decomposition of the iodostannous acid takes place according to the equation, $SnI_2.HI = SnI_2 + HI$, it follows that the iodostannous acid is stable at higher temperatures in contact with stronger acid. This is, of course, to be expected, since the stronger acid would exert greater pressure than would the weaker acid, against the entrance into the solution of new molecules of acid.

That decomposition of the solid iodostannous acid begins at temperatures lower than that at which it becomes wholly decomposed is shown by the falling off of curve No. 1 from the normal between 15° and 20°. That no definite temperature of transition exists between the two systems

$$\underset{\text{(Solid)}}{SnI_2.HI} + [\underset{\text{(Liquid)}}{SnI_2.HI} + HI + Aq] \rightleftarrows$$

$$\underset{\text{(Solid)}}{SnI_2} + [\underset{\text{(Liquid)}}{SnI_2 + SnI_2.HI} + HI + Aq]$$

is very evident, since the transformation of the first system into the second involves a great change in the nature of the solvent by increasing the concentration of the hydriodic acid and of the iodostannic acid, and by introducing a new factor, namely, stannous iodide. The transition is thus a gradual one, occurring over a considerable range of temperature. This is indicated by curve No. 1.

The falling solubility with increasing temperature from the point of complete change of the solid iodostannous acid into solid stannous iodide, must probably be taken to mean that even after the complete change has taken place in the solid forms, there remains in the solution more or less unchanged iodostannous acid. This becomes gradually transformed into stannous iodide and hydriodic acid, and the solution becomes supersaturated as to stannous iodide, which separates, causing the fall in solubility. This continues until all iodostannous acid is decomposed, or more probably, until further decomposition does not supersaturate the solution, and from that point the solubility increases

with the temperature. The curve does not, however, represent the true solubility of stannous iodide until all the iodostannous acid in the solution has been decomposed. This point may or may not agree with that at which the curve begins to rise.

Another peculiarity shown by the curves, which needs explanation, is the lack of coincidence between the portions of curves No. 1 and No. 2, which coincide as to temperatures. The experiments from which the two curves were obtained were made with the same solvent; namely, hydriodic acid of 39.60 per cent. It would seem at first sight that the portions of the two curves lying between 15° and 20° should coincide. The explanation of the lack of coincidence is, however, perfectly apparent. In making the solutions amounts of stannous iodide more than sufficient to saturate the solvent were used. The amounts were taken at random, so that in the two cases there were undoubtedly different excesses of stannous iodide. On cooling the solutions, iodostannous acid not only separates from the solution, but whatever excess of stannous iodide in the solid form may be present, provided it be not too great, is also converted into iodostannous acid. Thus the greater the excess of stannous iodide, the greater the demands made upon the solvent for hydriodic acid, and consequently the greater the weakening of the solvent as to hydriodic acid. Therefore, although both series of experiments were started with the same acid, the nature of the solvent will differ in the two cases after the cooling and the solubilities will naturally vary also.

It will be noticed that the break in the curve No. 2, at about 20° is caused by a sudden fall in solubility, while that in No. 3 at 1.5° is caused by a sudden rise in solubility. The explanation of this is entirely analogous to the foregoing. The direction of the change in solubility depends upon the relative solubilities of the two systems in whatever solvent may exist under the conditions.

As a matter of fact these sudden breaks are probably fictitious, and show in the curves only because sufficient time was not given at lower temperatures and at the temperatures of the breaks to attain perfect equilibrium, and also because the readings were not taken sufficiently close together.

The results of the work so far show mostly only qualitative

relationships. It is hoped soon to carry out a more exhaustive investigation upon the point, and also upon the similar chlorine and bromine compounds.

STANFORD UNIVERSITY,
July 20, 1897.

A COMPARISON OF VARIOUS RAPID METHODS FOR DETERMINING CARBON DIOXIDE AND CARBON MONOXIDE.

BY L. M. DENNIS AND C. G. EDGAR.

Received September 14, 1897.

THE value of gas analysis as an aid in the control and development of industrial processes is slowly being recognized by American manufacturers. Accompanying the increased use of this branch of analysis there seems to be, however, a tendency to adopt certain faulty methods of work to which it may be well to call attention. In industrial analyses chief stress will naturally be laid upon rapidity, and the accuracy demanded of the chemist will depend upon the nature of the work in hand. For example, in two processes in which carbon dioxide is regularly determined, it is sufficient in one case that the results be correct only within the range of one per cent., while in the other they should vary not more than one-tenth of one per cent. from the truth. In many cases, however, the analyst seems to be inclined to adopt some one form of apparatus and some one rapid method for the determination of each constituent and to adhere to this apparatus and method no matter what may be the conditions. Under such circumstances it is to be expected that the results obtained by different chemists on the same sample may show wide variations and even that the analyses of a single chemist, if his methods are not suited to the particular case in hand, may give rise to false deductions and cause financial loss to his employers. Difficulties similar to these were apparent, some years ago, in the analysis of iron and steel, and led to careful comparisons of the various methods by different chemists and to the development of standard methods of analysis. It was with the idea of making a beginning toward a similar comparison of some of the better known methods of gas analysis and of determining their relative accuracy and of ascertaining within what limits they might be relied upon, that Mr. Edgar undertook the

work described below. It is not claimed that the results show the absolute accuracy of the different methods, but they doubtless give quite closely their relative accuracy and the time which the average chemist would need for the various determinations.

The receiver for holding the gas mixtures to be analyzed consisted of a thick-walled, round-bottomed flask of about 700 cc. capacity. Into the neck of the flask was inserted a two-hole rubber stopper carrying two capillary glass tubes, one of these tubes ending just below the stopper and the other extending to the bottom of the flask. After firmly wiring the stopper, the flask was inverted and supported in a ring stand. The shorter capillary tube was connected by heavy rubber tubing with a level bottle containing about 800 cc. of mercury. The longer tube was bent in such a manner that it could easily be connected with the capillary of a Hempel gas burette. In collecting the samples for analysis, the air in the flask was first completely displaced by mercury from the level bottle and then measured portions of the gases to be mixed were run in through the longer capillary from a Hempel gas burette, this latter also containing mercury as the confining liquid. The flask was then shaken for five minutes and allowed to stand for some time, so that the gases might thoroughly mix. The gas mixture was at all times kept under a pressure slightly greater than that of the atmosphere, so as to prevent the possible entrance of air.

DETERMINATION OF CARBON DIOXIDE.

The gas mixture to be analyzed was prepared by mixing known volumes of air from outside the laboratory and carefully washed carbon dioxide prepared in a Kipp apparatus. The oxygen and nitrogen which might be contained in the carbon dioxide were not determined because the absolute accuracy of the different methods was in this work only of minor importance. Different mixtures of 500 cc. each were prepared, containing by measurement twenty, thirty, and forty per cent. of carbon dioxide. The solution of potassium hydroxide used for absorbing the carbon dioxide had the concentration recommended by Clemens Winkler;[1] namely, one part potassium hydroxide to four parts of water. The different forms of apparatus used were those devised by Honigmann, Bunte, Orsat, Elliot, and Hempel.

[1] Winkler: Lehrbuch der technischen Gasanalyse, 2te Auflage, 1892, p. 68.

Water was used in every case as the confining liquid. After each determination every measuring burette was rinsed with dilute hydrochloric acid to remove any potassium hydroxide that might accidentally have been introduced.

HONIGMANN'S BURETTE.

This was described to Professor Clemens Winkler by Moritz Honigmann, in a letter dated March 15, 1881. The method of using it which we adopted was that given by Winkler,[1] except that in filling the burette with the gas, instead of aspirating the gas through the burette until the air has been completely displaced, the burette was first filled with water which had been saturated with the gas, and the water was then displaced by gas from the receiver.

Sample No.	Carbon dioxide. Per cent.	Check result with Hempel's apparatus. Per cent.	Results with Honigmann's apparatus. Per cent.	Time in minutes.
I.	20	19.9	19.6	10 : 00
			18.9	9 : 00
			19.1	9 : 30
II.	20	19.85	19.8	7 : 10
			19.8	6 : 30
			19.7	6 : 15
III.	20	20.1	20.0	6 : 00
			19.8	5 : 30
			19.8	5 : 00
IV.	30	29.9	29.2	6 : 30
			29.1	7 : 10
			29.0	5 : 40
V.	30	29.7	29.4	5 : 00
			29.5	5 : 00
			29.6	5 : 30
VI.	30	29.6	29.3	5 : 30
			29.4	5 : 15
			29.5	5 : 00
VII.	40	39.9	39.2	6 : 10
			39.0	6 : 00
			38.9	5 : 30
VIII.	40	40.1	39.7	6 : 00
			39.8	6 : 15
			39.2	5 : 35
IX.	40	39.9	38.9	5 : 30
			39.5	6 : 00
			39.4	6 : 10

[1] Winkler : Lehrbuch der technischen Gasanalyse, 2te Auflage, 1892, p. 82.

AVERAGES WITH HONIGMANN'S APPARATUS.

Per cent.	Per cent.
20	19.6
30	29.2
40	39.31

BUNTE'S BURETTE.[1]

Method of use was as described by Winkler, p. 84.

Sample No.	Carbon dioxide. Per cent.	Check result with Hempel's apparatus. Per cent.	Results with Bunte's apparatus. Per cent.	Time in minutes.
X.	20	19.9	19.8	8:30
			19.7	8:15
			19.8	8:35
XI.	20	20.1	19.8	8:30
			19.7	8:25
			20.1	8:50
XII.	20	20.0	19.8	8:10
			19.6	....
			19.8	8:00
XIII.	30	29.9	29.7	8:20
			29.8	8:45
			29.6	8:00
XIV.	30	30.1	29.9	8:20
			29.7	8:15
			30.0	8:40
XV.	30	29.8	29.8	8:10
			29.6	8:35
			29.7	8:15
XVI.	40	40.0	38.9	8:15
			39.3	8:00
			39.5	8:10
XVII.	40	39.8	39.5	8:25
			39.3	8:30
			39.5	8:00
XVIII.	40	39.9	39.3	8:00
			39.4	8:15
			39.5	8:25

AVERAGES WITH BUNTE'S APPARATUS.

Per cent.	Per cent.
20	19.8
30	29.7
40	39.33

[1] *Journal für Gasbeleuchtung*, 1877, p. 447.

ORSAT'S APPARATUS.

The form of this apparatus which we employed was that now made by Robert Muenckē, Berlin, and it was used in the manner described by Winkler, p. 89.

Sample No.	Carbon dioxide. Per cent.	Check result with Hempel's apparatus. Per cent.	Results with Orsat's apparatus. Per cent.	Time in minutes.
XIX.	20	19.8	19.7	7:00
			19.6	8:00
			19.8	7:45
XX.	20	19.9	19.6	8:15
			19.7	8:00
			19.6	7:15
XXI.	20	19.8	19.5	8:10
			19.6	8:00
			19.5	7:50
XXII.	30	29.8	29.2	6:50
			29.3	7:00
			29.0	6:40
XXIII.	30	29.7	29.2	7:00
			29.3	7:15
			29.3	8:00
XXIV.	30	29.9	29.3	7:00
			29.4	7:35
			29.3	7:40
XXV.	40	40.0	39.2	7:00
			39.1	6:10
			39.2	6:00
XXVI.	40	39.9	39.3	5:45
			39.2	6:00
			39.3	6:10
XXVII.	40	39.8	39.4	6:50
			39.3	7:10
			39.4	7:00

AVERAGES WITH ORSAT'S APPARATUS.

Per cent.	Per cent.
20	19.62
30	29.45
40	39.46

ELLIOT'S APPARATUS.

This apparatus is described in the *Chem. News*, *1881*, **44**, 289.

Sample No.	Carbon dioxide. Per cent.	Check result with Hempel's apparatus. Per cent.	Results with Elliot's apparatus. Per cent.	Time in minutes.
XXVIII.	20	19.8	19.7	6:50
			19.6	7:10
			19.7	7:00
XXIX.	20	19.9	19.7	....
			19.6	....
			19.5	....
XXX.	20	20.0	19.8	....
			19.5	....
			19.8	....
XXXI.	30	30.0	29.6	8:15
			29.5	8:10
			29.6	8:40
XXXII.	30	28.9	29.5	....
			29.7	....
			29.6	....
XXXIII.	30	29.9	29.4	7:10
			29.6	7:00
			29.5	6:50
XXXIV.	40	39.9	39.2	6:20
			39.3	6:15
			39.0	6:10
XXXV.	40	39.9	39.5	6:50
			39.4	7:00
			39.8	6:35
XXXVI.	40	39.8	39.3	7:00
			39.6	6:50
			39.5	6:10

AVERAGES WITH ELLIOT'S APPARATUS.

Per cent.	Per cent.
20	19.66
30	29.55
40	39.41

HEMPEL'S APPARATUS.

The gas burette was that shown in Fig. 17 of the English edition of Hempel's Methods of Gas Analysis. The absorption pipette shown in Fig. 21, *b*, was employed, this being filled with iron wire gauze and potassium hydroxide, as described on page 157.

In some of the determinations given below the water was allowed to run down the walls of the burette for the usual time, three minutes. In others this time was shortened to one-half a minute to see whether the work could be hastened without too great a sacrifice of accuracy.

Sample No.	Carbon dioxide. Per cent.	Results with Hempel's apparatus. Per cent.	Time allowed for running down of water.	Time in minutes.
I.	20	19.9	3 min.	10:00
II.	20	19.85	3 "	9:00
III.	20	20.1	3 "	10:00
X.	20	19.9	3 "	8:50
XI.	20	20.1	3 "	9:00
XII.	20	20.0	3 "	8:40
XIX.	20	19.8	30 sec.	4:00
XX.	20	19.9	30 "	4:15
XXI.	20	19.8	30 "	4:09
XXVIII.	20	19.8	30 "	4:00
XXIX.	20	19.9	30 "	4:10
XXX.	20	20.0	30 "	.....
IV.	30	29.9	3 min.	9:00
V.	30	29.7	3 "	9:00
VI.	30	29.6	3 "	9:00
XIII.	30	29.9	3 "	9:00
XIV.	30	29.9	3 "	9:50
XV.	30	30.1	3 "	9:00
XXII.	30	29.8	30 sec.	3:30
XXIII.	30	29.7	30 "	4:00
XXIV.	30	29.9	30 "	3:50
XXXI.	30	30.0	30 "	4:00
XXXII.	30	29.9	30 "	4:10
XXXIII.	30	29.9	30 "	4:05
VII.	40	39.9	3 min.	9:00
VIII.	40	40.1	3 "	8:45
IX.	40	39.9	3 "	9:00
XVI.	40	40.0	3 "	8:50
XVII.	40	39.8	3 "	9:00
XVIII.	40	39.9	3 "	9:00
XXV.	40	40.0	30 sec.	4:00
XXVI.	40	39.9	30 "	3:30
XXVII.	40	39.8	30 "	4:10
XXXIV.	40	39.9	30 "	4:15
XXXV.	40	39.9	30 "	4:25
XXXVI.	40	39.8	30 "	6:15

AVERAGES WITH HEMPEL'S APPARATUS.

Per cent.				Per cent.
20	3 min.	running	down	19.97
20	30 sec.	"	"	19.87
30	3 min.	"	"	29.85
30	30 sec.	"	"	29.87
40	3 min.	"	"	39.93
40	30 sec.	"	"	39.89

DETERMINATION OF CARBON MONOXIDE.

The gas mixture to be analyzed consisted of a mixture of nitrogen and carbon monoxide, the latter being prepared from oxalic acid. Mixtures containing by measurement three, nine, and fifteen per cent. of carbon monoxide were used. The gas was absorbed by means of a hydrochloric acid solution of cuprous chloride. For preparing this solution of cuprous chloride, we have used for some years in this laboratory the method which was suggested by Sandmeyer,[1] and which has been found superior to any other that we have tried.

The methods for determining carbon monoxide which were compared were those of Orsat, Elliot, and Hempel. After absorption by the cuprous chloride, the gas residue was always treated with potassium hydroxide, to free it from any acid vapors, before the final reading was made.

ORSAT'S APPARATUS.

The gas sample was passed into the cuprous chloride tube and allowed to remain there for three minutes. It was then run back and forth from the burette for two minutes longer. Then it was passed into the potassium hydroxide tube and finally brought into the burette and measured.

[1] Sandmeyer: *Ber. d. chem. Ges.*, 17, 1633. Twenty-five parts of crystallized copper sulphate and twelve parts of dry sodium chloride are placed in fifty parts of water and heated until the copper sulphate dissolves. (Some sodium sulphate may separate out.) 100 parts of concentrated hydrochloric acid and thirteen parts of copper turnings are then added and the whole is boiled in a flask until decolorized. Platinum foil will hasten the process. The solution is kept in glass-stoppered bottles until wanted.

Sample No.	Carbon monoxide. Per cent.	Results with Orsat's apparatus. Per cent.	Time in minutes.
		2.3	13 : 00
I.	3	2.5	12 : 10
		2.2	11 : 00
		2.1	13 : 00
		2.0	12 : 10
II.	3	2.3	11 : 50
		2.7	12 : 30
		2.4	11 : 15
		8.4	14 : 00
III.	9	8.5	10 : 10
		8.4	10 : 30
		8.6	10 : 00
		8.5	15 : 40
IV.	9	8.4	11 : 00
		8.5	10 : 30
		8.7	10 : 45
		14.5	14 : 00
		14.2	15 : 00
V.	15	14.4	13 : 50
		14.6	14 : 10
		14.7	16 : 10
VI.	15	14.3	15 : 40
		14.6	14 : 00
		14.4	15 : 15

AVERAGES WITH ORSAT'S APPARATUS.

Per cent.	Per cent.
3	2.31
9	8.5
15	14.4

ELLIOT'S APPARATUS.

The gas was here also treated with potassium hydroxide after the absorption of the carbon monoxide.

Sample No.	Carbon monoxide. Per cent.	Results with Elliot's apparatus. Per cent.	Time in minutes.
		2.4	10 : 00
		2.3	10 : 30
VII.	3	2.4	9 : 50
		2.1	10 : 10
		2.5	10 : 10
		2.3	11 : 00
VIII.	3	2.4	10 : 50
		2.0	10 : 30
		8.4	11 : 00
		8.5	10 : 50
IX.	9	8.3	11 : 40
		8.0	10 : 20
		8.4	13 : 00
		8.0	12 : 10
X.	9	7.9	11 : 50
		8.3	10 : 00
		14.1	14 : 10
		13.9	15 : 00
XI.	15	14.0	13 : 50
		14.4	14 : 30
		14.0	14 : 00
XII.	15	14.4	13 : 10
		13.8	13 : 40
		14.2	14 : 10

AVERAGES WITH ELLIOTT'S APPARATUS.

Per cent.	Per cent.
3	2.3
9	8.2
15	14.1

HEMPEL'S APPARATUS.

Two double gas pipettes were employed, the one which was used second containing a fresh solution of cuprous chloride.[1] The gas was passed into the first pipette, which was then shaken for two minutes; then into the second pipette and shaken for three minutes; then into a potassium hydroxide pipette, and finally into the burette, where it was measured.

[1] Hempel: Methods of Gas Analysis, p. 161.

Sample No.	Carbon monoxide. Per cent.	Results with Hempel's apparatus. Per cent.	Time in minutes.
		3.2	10 : 10
		3.0	9 : 50
XIII.	3	2.9	10 : 00
		2.8	9 : 40
		2.8	10 : 00
XIV.	3	3.0	9 : 50
		2.9	9 : 30
		2.8	9 : 20
		8.7	9 : 30
XV.	9	8.8	9 : 10
		8.9	9 : 15
		8.8	9 : 30
		8.8	9 : 10
XVI.	9	9.0	8 : 50
		8.9	9 : 00
		8.7	8 : 45
		14.7	9 : 00
XVII.	15	14.6	8 : 40
		14.8	8 : 50
		14.5	9 : 00
XVIII.	15	14.7	8 : 30
		14.8	9 : 00

AVERAGES WITH HEMPEL'S APPARATUS.

Per cent.	Per cent.
3	2.9
9	8.85
15	14.77

The above results show that in the determination of carbon dioxide all of the five methods tested are accurate to within less than one per cent., and all except Honigmann's, to within one-half of one per cent., provided the amount of carbon dioxide present does not exceed thirty per cent. The most exact results in every case, however, are those obtained with Hempel's apparatus, and when the carbon dioxide is as high as forty per cent., this is the only method in which the error does not exceed five-tenths per cent. As regards speed, the Hempel method, with only thirty seconds allowed for the running down of the water, seems to have been the shortest, but was closely followed by the

Honigmann method. Attention may also be called to the fact that while in the methods of Honigmann, Orsat, and Hempel, the same potassium hydroxide is used repeatedly, in the Bunte and Elliot methods the reagent cannot be used twice, these methods being thus extremely wasteful.

In the determination of carbon monoxide the superiority of the Hempel method, both in accuracy and speed, is even more marked. Better results than those cited can be obtained with both the Orsat and Elliot apparatus but only by greatly prolonging the time.

CORNELL UNIVERSITY,
JULY, 1897.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY No. 23.]

THE ELECTROLYTIC DETERMINATION OF CADMIUM.

BY DANIEL L. WALLACE AND EDGAR F. SMITH.

Received September 9, 1897.

ABOUT a year ago Max Heidenreich[1] published an article in which he reviewed methods proposed by one of us (S) for the electrolytic determination of certain metals. In some instances he confirmed the observations of Smith, but in most cases differed with him. Recently S. Avery and Benton Dales[2] announced that so far as the determination of cadmium was concerned their "result was in complete harmony with the experiments of Heidenreich." In consequence of these experiences with the electrolytic methods suggested by Smith for the determination of cadmium, we have repeated them and offer new results obtained by us.

It was in 1878[3] that Smith stated that "0.1450 gram of cadmium oxide was dissolved in acetic acid, the excess of the latter expelled upon a water-bath and the platinum crucible then about half filled with water, and * * * connected with the negative pole of a two-cell Bunsen battery * * * . The deposition of the cadmium was regular * * * a perfectly crystalline, grayish white layer." The precipitation was complete in about three hours. The experiment was repeated, but a bichromate battery was substituted for the Bunsen cells. At the time when these

[1] *Ber. d. chem. Ges.*, **29**, 1585.
[2] This Journal, **19**, 380.
[3] *Proc. Am. Phil. Soc.*, November, 1878.

trials were made, current strength in definite units was not given, hence subsequent workers have met with difficulty in repeating some of the early work, and perhaps that may account for the failure to precipitate cadmium from the solution of its acetate. We have sought to obtain the original working conditions given by Smith, have stated them in definite units, and append results obtained by their observance.

Experiment 1.—0.1329 gram of cadmium oxide was dissolved in acetic acid, the solution was evaporated to dryness, and the residue dissolved in thirty cc. of water. The liquid was then heated to 50° C., and electrolyzed with a current of 0.02 ampere for thirty-seven sq. cm. of cathode surface. Voltage, 3.5. The metal was completely precipitated in four hours. It was crystalline and perfectly adherent. There was no evidence of sponginess. The hot, acid liquid was siphoned off and replaced by water without interrupting the current. We found that the period of precipitation could be diminished and very good results be obtained by adding one gram of ammonium acetate to the solution when the current had acted for an hour. The quantity of metallic cadmium present in this particular experiment was 0.1162 gram, while that actually found equaled 0.1158 gram.

Experiment 2.—0.1332 gram of oxide, treated precisely as outlined in Experiment 1, gave 0.1164 gram of adherent, crystalline metal instead of 0.1165 gram.

With these results before us we see no cause why the deposition of this metal from its acetate solution should be condemned. Neumann[1] mentions it as being possible, and Yver[2] even used an acetate solution in the electrolytic separation of cadmium from zinc.

Smith[3] published experiments made by him on the precipitation of cadmium from solutions containing free sulphuric acid. As this method seems not to have proved satisfactory in the hands of Heidenreich, and of Avery and Dales we have repeated the work and offer the following experiments as evidence in favor of the Smith method:

Experiment 1.—0.1270 gram of cadmium oxide was dissolved in two cc. sulphuric acid, sp. gr. 1.09, and the solution then

[1] Theorie und Praxis der analyt. Elektrolyse, p. 129.
[2] *Bull. Soc. Chim.*, **34**, 18.
[3] *Am. Chem. J.*, **2**, 41.

made up with water to thirty cc. It was heated to 50° C., and electrolyzed for a period of four and one-half hours with a current of 0.08 ampere for thirty-seven sq. cm. cathode surface. Voltage 2.5. The deposit weighed 0.1105 gram instead of 0.1111 gram. It was crystalline and adherent. Tendency to sponginess was not observed. The acid liquid was siphoned off before interrupting the current. The filtrate showed no signs of cadmium when tests were made for it.

Experiment 2.—In this trial 0.1358 gram of cadmium oxide was dissolved and treated as in Experiment 1. The deposit of metal weighed 0.1181 gram instead of 0.1188 gram.

We have never experienced any difficulty in the application of this method, and are also pleased to observe that Neumann[1] gives an example confirming the early recommendation of Smith. It is this: "die Lösung von 0.3 gram Kadmium sulfat in 150 cc. Wasser mit 1 bis 2 cc. verdünnter Schwefelsäure versetzt, wird auf 70 bis 80 Grad C., erwärmt und bei diesem Temperatur durch Ströme von 0.6 bis 1 Ampere zersetzt. Die Spannung schwankt ..... zwischen 2.5 bis 5 Volt ..... Der Niederschlag ist silberweiss."

Our experiences with the precipitation of cadmium from a phosphoric acid solution will be reserved for a subsequent communication.

We regard the double cyanide solution[2] as the best adapted for the deposition of cadmium. Further evidences of this are the many atomic weight determinations made of this metal, in which this particular solution was employed.[3]

The first suggestion for the electrolytic separation of copper from cadmium was also made by Smith.[4] He demonstrated that in the presence of free nitric acid copper was deposited in satisfactory form, while the cadmium continued in solution. Heidenreich,[5] in speaking of this method, which has received frequent confirmation, remarks: "eine Reihe von Versuchen, Kupfer von Kadmium aus einer freie Saltpetersäure enthaltenden Lösung zu trennen, führten zu keinem befriedigenden Ergeb-

1 *Loc. cit.*
2 *Ber. d. chem. Ges.*, **25**, 779.
3 *Ztschr. anorg. Chem.*, **1**, 364; This Journal, **18**, 1022.
4 *Am. Chem. J.*, **2**, 43.
5 *Loc. cit.*

nisse." In reply to this we offer the following experiments:

Experiment 1.—To a solution containing 0.3893 gram of copper sulphate (= 0.0988 gram of copper) and 0.1152 gram of cadmium oxide (= 0.0985 gram of cadmium) were added two cc. of nitric acid, sp. gr. 1.43. The total dilution of the solution equaled 100 cc. It was heated to 50° C., and electrolyzed with a current $N.D._{100} = 0.10$ ampere. Voltage 2.5. The metal was completely precipitated in three hours. It was bright in color and satisfactory in every respect. It weighed 0.0988 gram and did not contain cadmium.

Experiment 2.—A solution containing the same quantity of copper and 0.1203 gram of cadmium oxide, when treated exactly as in Experiment 1, gave 0.0987 gram of copper. It was free from cadmium.

To these results we would add the observation of Neumann:[1] "Am einfachsten is zur trennung von Kupfer und Kadmium immer die Verbindung der mit *freier Saltpetersäure* versetzten Lösung beider Salze."

Heidenreich maintains that the separation of copper from cadmium succeeds "sicherer aus einer mit *Schwefelsäure* versetzten Lösung." This solution had been previously recommended by Smith,[2] and his observations were confirmed by Freudenberg.[3]

The results recorded in the preceding paragraphs justify us in saying that cadmium can be successfully determined electrolytically when working either with its acetate or sulphate, and that its separation from copper in the presence of nitric acid is in every respect satisfactory.

The failure of Heidenreich to precipitate uranic oxide by means of the current will be considered later.

UNIVERSITY OF PENNSYLVANIA.

ON THE REACTIONS BETWEEN MERCURY AND CONCENTRATED SULPHURIC ACID.

BY CHARLES BASKERVILLE AND F. W. MILLER.

Received September 16, 1897.

MANY text-books class the reactions between copper and concentrated sulphuric acid along with mercury and sul-

[1] Elektrolyse, p. 169.
[2] See Electrochemical Analysis, 2nd. Ed., p. 108.
[3] *Ztschr. phys. Chem.*, 12, 97.

phuric acid, stating merely that a sulphate of copper or mercury is formed with the evolution of sulphur dioxide.

In other communications[1] one of us, (Baskerville) has shown that while the formula

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O,$$

expresses in fact the main reaction when these two substances are brought together, even at different temperatures, that only at 270° C., or higher, is that reaction unaccompanied with very important and complex secondary reactions. In preparing sulphur dioxide, by heating together copper and concentrated sulphuric acid, invariably a black or brown material discolors the colorless acid. This dark substance is, in the main, cuprous sulphide.

Not finding the reaction between mercury and concentrated sulphuric acid worked out in detail in any of the literature at our command and since so much wrong data have been recorded concerning copper under similar conditions, it was deemed advisable to study this reaction at different temperatures.

The reaction is by no means like that of copper. The primary reaction depends upon the preponderance of mercury or acid, the temperature, and the time during which it is allowed to continue.

If the mercury be in larger amounts than the acid, invariably almost pure mercurous sulphate is produced :

$$2Hg + 2H_2SO_4 = Hg_2SO_4 + SO_2 + 2H_2O.$$

It will be well to state here that the mercurous sulphate so produced is a white crystalline substance and not black, as stated in Roscoe and Schorlemmer's Treatise on Chemistry.[2]

Series of experiments in duplicate were carried out at different temperatures when the acid was in large excess. A qualitative experiment showed that mercury decomposed concentrated sulphuric acid at the ordinary atmospheric temperature, about 20° C. This experience is contrary to that stated in a number of text-books. Experiments carried out at 100° C. upon a water-bath, lasting during twenty hours, in apparatus especially arranged to insure only the presence of dust-free, dry air

[1] This Journal, 17, 904, and 18, 942.

[2] Vol. II, Part I, p. 401.

showed that about one-fifth of the mercury had entered into the reaction. Ten grams of the mercury and from fifty to 100 grams acid were used. Expecting the results to exhibit this reaction,

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O,$$

we were surprised to find so much less sulphur dioxide evolved than should have been. The crystalline sulphate produced gave 20.75 per cent. SO_4, which is very near 19.35 calculated for mercurous sulphate. Again, at 150° C., when the flask containing the mercury and acid was kept at a practically constant temperature by being immersed in a sulphuric acid bath for two hours, the amount of sulphur dioxide evolved was much below the theoretical. At least half of the mercury in each of these experiments was dissolved. The white crystalline layer of sulphate which separated out as the amount of metallic mercury decreased was augmented by another layer, which had been in solution, when the acid became cool. Both were crystalline, but while the latter was powdery the former was composed of needle-like crystals. To avoid the formation of the basic sulphate, $HgSO_4.2HgO$, which was always produced in our efforts to wash out the remaining acid with water, we used ninety-five per cent. alcohol. Four washings were sufficient; in fact, on further washing even with alcohol some basic sulphate was formed. On analysis of this alcohol-washed substance, which had been dried to a constant weight at 100° C., we obtained:

	Calculated for $Hg_3(SO_4)_2$, or $Hg_2SO_4.HgSO_4$.	Found.
SO_4	24.24	23.96 24.27
Mercury (-ous)	50.38	50.27

At 200° C. the percentage of mercurous mercury dropped to 40; at 250° C. still lower, showing a steady decrease in the amount of mercurous sulphate produced as the temperature increased. When the acid was boiled and the mercury poured in, the crystalline compound gave 32.91 per cent. of sulphur tetroxide when mercuric sulphate contains 32.43 per cent. Evidently some of the acid was not removed by the washing with alcohol.

It was desirable to determine whether the primary reaction took place in steps, *e. g.*, if the metal liberated hydrogen, which

in the nascent state attacked the remaining sulphuric acid with the production of sulphur dioxide, such having been recorded by some authors to be the case in the reaction between copper and sulphuric acid. Careful experiments at different temperatures, 150° and 200° C., were carried out in an atmosphere of carbon dioxide free from air. One hundred cc. of the gases given off and collected over a ten per cent. solution of sodium hydroxide gave not a trace of hydrogen. The sulphuric acid in this case is evidently reduced directly by the metal. No sulphide was produced, nor any free sulphur.

If portions of the crystalline compound, produced by the treatment of mercury with concentrated sulphuric acid rendered free of acid by washing with alcohol and dried at 100° C., be again treated with acid in similar apparatus, sulphur dioxide is evolved in proportion to the amount of mercurous sulphate there is present. If mercuric sulphate be treated with the acid no sulphur dioxide is evolved. In fact, if a prepared mixture of mercurous and mercuric sulphates in varying proportions, or any of the crystalline compounds obtained in any of the experiments cited, except that produced by the boiling acid, be treated with fresh acid and heated until the gas evolved ceases to bleach a weak potassium permanganate solution, the crystalline residue then obtained is mercuric sulphate.

Although the relative yield of sulphur dioxide is less, the treatment of mercury with concentrated sulphuric acid has been recommended for classroom experiment on account of neatness and freedom from black residue, which in the case of copper is oftentimes unintelligible to the ordinary student. A slight objection may be urged against this use on account of the volatility of the metallic mercury at the temperature of reaction. Faraday has shown that in spite of its high boiling-point, mercury volatilizes at the ordinary temperatures. One of us (Baskerville) has had this fact to contend with in several cases where this method of evolving sulphur dioxide was made use of in quantitative work.

In the experiments given all materials used were pure. The concentrated sulphuric acid was of 1.84 sp. gr. The mercury was purified according to Lothar Meyer's method[1] by allowing

[1] *Ztschr. anal. Chem.*, **2**, 241.

the distilled metal to flow in a thin stream first through a column of dilute nitric acid, then dilute sulphuric, to dissolve out all lead and tin, finally washed and dried. All apparatus was most carefully cleansed, and when necessary moisture-free and proved to be air-tight.

UNIVERSITY OF NORTH CAROLINA,
July, 1897.

ON THE DETERMINATION OF FAT AND CASEIN IN FECES.

BY HERMAN POOLE.

Received August 24, 1897.

HAVING been called upon to make some examinations of feces from children in connection with the clinical experiments on the Prof. Gaertner mother-milk now being carried on with satisfactory results at the German Polyclinic on Seventh Street, New York City, I began by looking up what had been done on the subject previously. To my surprise I found nothing at all which would give even a fairly approximate idea of the percentage of fat and casein. After consulting all the authorities I could find, I saw that I must work out a new or a fuller method than any previously used.

The problem to solve was this: A certain child takes per day a definite quantity of milk of known composition. It digests a portion of this and passes off the balance undigested. This milk contains fat and casein. How much fat and how much casein pass through undigested, and from this how much of the milk is assimilated?

Of course, one of the first books suggested to an American would be Flint's Physiology, since Flint has done considerable work on this kind of material several years ago. An examination of his work, however, showed that the methods he used and the special objects he had in view were entirely unsuited and foreign to the work I intended. He operated on the feces of adults, and more particularly to discover and extract the unknown and undescribed constituents rather than to actually make accurate determinations of the common and known ones. Besides, the chemical methods in use in his day are to a considerable extent supplanted by more accurate and modern methods.

Papers have been published and articles written on the analyses of feces for certain purposes by Rubner, Camerer, Prausnitz, Mayer, and Constanidini in the *Zeitschrift für Biologie* in most of the volumes since 1879, and by Malfatti and Strumpell,[1] but none of these in any way outline methods which would be used in my investigation. The fullest account given is that by Prausnitz,[2] in which he sums up what has been done and gives the result of the most recent work up to that time.

But all these methods are insufficient, not carrying the analysis far enough. Neither attempts to separate the fat or the casein in a state approaching freedom from other allied or commixed substances. All give the results of imperfect separations.

The fat determinations are all made by drying the material at 100° and then extracting with ether. This ether extract is evaporated; the residue is weighed and calculated as fat. This would be a very simple and easy method, but, unfortunately, it is not correct and can give only misleading deductions. In addition to the fatty matter, ether dissolves cholesterol and some of the bile and other products. The proportion of cholesterol is not constant, varying from twenty-five to seventy-five per cent.; the amount contained varies from day to day with the same child, and even varies with the successive passages. Still greater then must be the variation with different children. The proportion of the other substances is small and may be neglected ordinarily. It will be easily seen, therefore, that deductions based on such determinations must be faulty.

In the determination of casein no satisfactory method has yet been devised that I know of. The authorities cited have taken the ether extract, the water extract, and the alcohol extract; the residue was then treated by some method for determining the nitrogen and it was given as such, no attempt being made to separate the nitrogen of the food, digested or undigested, from that of extraneous bodies which might be present. This method is even more faulty than the fat determination. It shows the amount of nitrogen passing off through this channel but gives no idea as to the form in which it occurs.

1 *Konig's Chem. der Mensch. Nahrung und Genuss*, I, 37 and 46.
2 *Ztschr. für Biol.*, *1894*, pp. 328 *et seq.*

The insoluble residue, after the three menstrua above mentioned have been used, contains the insoluble casein, the insoluble fatty acid compounds (usually lime, alumina, and iron as bases) and the broken down epithelium cells gathered from the whole length of the intestinal tract. This waste epithelium is at times quite an important factor and is always present in an appreciable degree as can be seen by a microscopic examination. The fatty acid compounds, of course, contain no nitrogen. The three menstrua fortunately remove most of the numerous nitrogenous substances present in the original material, leaving only a small quantity not in the epithelium cells or in the casein; so that it may be considered that the remaining undissolved mass consists substantially of the last two.

The problem then becomes one of separating the cholesterol from the fat and the casein from the epithelium cells and other foreign matter.

First, separation of the fat and cholesterol. The ether extract containing these two and the coloring matter from the bile is sometimes yellow, sometimes brown or greenish. It always contains some substances insoluble, or difficultly soluble, in alcoholic potash, which is used for saponification and solution of the fat and cholesterol.

The ether extract is evaporated nearly dry at 100° C. and then heated at 110° C. till dry. This heating to 100° is necessary, since, although ether is used as a solvent, this ether always contains a little water, sometimes more than will be driven off at 100°. The residue is then saponified with alcoholic potash, which usually leaves only a small portion undissolved. When thoroughly saponified, water is added and the whole boiled to expel the alcohol. Then more water is added, if needed, and the solution filtered. The filtrate should be clear and opalescent, but is usually colored. Now pour the filtrate into a separatory globe or cylinder and agitate thoroughly with an equal bulk of ether. Allow to stand and separate. Draw off the liquids separately and again treat the heavier one with ether as before. A further treatment with ether usually reveals only slight traces of cholesterol and need not be made. The liquid thus freed from cholesterol is now evaporated nearly dry and dissolved in water. It contains the fat acids, which may be determined by any of the usual

methods, and multiplication by the proper factor will give the amount of butter fat originally contained in the feces as such.

Secondly, the separation of the casein from the other substances. This is a difficult separation. None of the strong solvents, alkalies, strong acids, etc., can be used as they destroy both, or while attacking one, attack the other. Neutral salts are not satisfactory for dissolving insoluble casein since large quantities of liquid must be used, and even then a second treatment with the same solvent will usually dissolve more.

The method which I finally adopted, while not entirely satisfactory, still gives results far nearer the truth than any of the published ones and, at least for the purpose in view, comparable results.

The feces are extracted in succession by ether, water, and alcohol, and then dried. The residue is digested for several hours (usually over night) in a mixture of thirty parts hydrochloric acid and seventy parts water at a temperature of about 50° C. This dissolves the casein and leaves the epithelium débris and other substances. The fatty acid compounds are of course decomposed, but do not influence the result at all. Hydrochloric acid is more satisfactory than the neutral salts and gives fairly concordant results on duplicate trials. After cooling sufficiently, the liquid is filtered off, evaporated, and the nitrogen determined by the Kjeldahl method. From this the quantity of casein is calculated and the percentage determined.

In a careful, thorough analysis the quantity of fatty acids in the insoluble soap would of course be determined, but with my investigation this is not necessary, as they usually represent digested or partially changed fats, and I am looking only for the undigested portions.

My results of course are much lower than would be obtained by the old method, but I claim they are nearer the truth and perfectly comparable among themselves. They certainly do show more nearly the composition of the material examined and furnish a better guide as to the workings of the food on the child and the child on the food.

No percentage results are given in this paper as no work has yet been done on perfectly healthy children, and such work is needed as control.

The investigation will be pursued and if possible more satisfactory methods devised. Any suggestions from chemists having experience in this line will be thankfully received.

THE PRINCIPAL AMID OF SUGAR-CANE.

By Edmund C. Shorey.

Received October 4, 1897.

IT has been more than forty years since Lawes and Gilbert pointed out that in plants used as feed for stock, part of the nitrogen exists in the amid form. Since then several schemes of analysis have been devised by which to determine the amounts of different forms of nitrogen in plants, and numbers of analyses have been published in accordance with these schemes, so that it has come to be generally accepted by chemists that a part of the nitrogen of all plants, in the growing stage at least, is in the amid form. E. Schulze, who has done more than anyone else to advance our knowledge of the forms in which nitrogen exists in plants, states that the amid compounds vary with different plants, and also with the age and condition of the plant.

In 1892 I determined the total and albuminoid nitrogen content of a number of samples of mature sugar-cane. In the samples then examined I found the albuminoid to be about ninety per cent. of the total nitrogen. Analyses made later of another and less mature variety of cane, showed this non-albuminoid nitrogen to be sometimes as high as twenty-five per cent. of the total nitrogen. The albuminoid nitrogen was determined by precipitating with cupric hydroxide, taking special precautions to prevent any decomposition of the albuminoids by preliminary heating. No attempt was made at that time to determine the character of the non-albuminoid nitrogen.

In January, 1894, a paper was read by W. Maxwell before the Louisiana Sugar Planter's Association on "Organic Solids not Sugar in Cane Juice." The matter of this paper was subsequently issued as a bulletin by the Louisiana Experiment Station. In this paper attention was drawn to the fact already noticed, that all plants contain at some period part of their nitrogen in the amid form: a fact well known to chemists, but apparently overlooked by sugar manufacturers. After giving a number of analyses of cane juice, in which the difference

between the total and albuminoid nitrogen was designated amids, Maxwell stated that the amid of cane juice was found to be asparagin, crystallized preparations of this body having been obtained. He made, however, no statements regarding the physical or chemical properties of the asparagin obtained, nor did he give any information as to how it was ascertained to be asparagin.

Some months after the publication of this paper, there was a discussion in the *Bulletin de l'Association des Chimistes de Sucrerie* between H. Pellet and W. Maxwell as to the possibility of the asparagin of cane juice affecting the polariscopic reading of such solutions. In view of this possibility I determined to make some preparations of the amid compound or compounds in cane juice, and ascertain the rotatory power of the same. This work was begun in January and continued until July of the present year, and covers every variation in age and condition of cane delivered at the mill this year, as well as some samples of very young cane.

As a result of this work I have found that the principal amid compound present in sugar cane is *not optically active*, and is *not asparagin*, but glycocoll or glycocin, an amid not heretofore known to occur in plants.

The method of separating the amid was that commonly used, *viz.*, precipitation with mercuric nitrate. To the juice obtained from the cane sample by pressure, a slight excess of lead subacetate was added, the liquid filtered, and to the filtrate an acid solution of mercuric nitrate was added, and the whole brought to faint acidity if strongly acid, by the cautious addition of caustic soda. The precipitate thrown down, which was white and flocculent, after being well washed, was decomposed by hydrogen sulphide. The filtrate from the mercuric sulphide, after being concentrated to a thin syrup, was allowed to stand, when abundant, well defined crystals were generally formed in thirty-six hours. The filtrate from the mercuric sulphide was always quite strongly acid, and the subsequent crystallization was found to be much more rapid, and the yield larger if the solution were neutralized with ammonia before concentration, and neutrality maintained during concentration by the continued addition of ammonia as the solution became acid again.

This addition of ammonia made no difference in the character of the crystalline body obtained. The crystals after separation from the mother-liquor were purified by recrystallizing twice.

The mercuric nitrate used was prepared as wanted by boiling mercury with an excess of nitric acid until no further reaction for mercurous nitrate was obtained. I have as yet made no analysis of the white insoluble precipitate which mercuric nitrate gives with the amid body in question.

The purified crystals were in the form of plates or four-sided prisms, belonging to the monoclinic system; glassy in appearance, quite hard, grating between the teeth and having a sweetish taste. They were soluble in cold water, but much more readily in hot, soluble in eighty per cent. alcohol, but insoluble in ether. In all, fifteen preparations of these crystals have been obtained, and in all cases the physical properties of the crystals and the chemical properties of the solution have been the same.

The mother-liquor from the crystals was found to contain other nitrogenous bodies not readily obtained in a crystalline form, the nature of which has not yet been ascertained; but they are comparatively small in amount, and, since nearly the whole of the bodies precipitated from cane juice by mercuric nitrate can be obtained in a single crystalline form having the properties of an amid, it is quite justifiable to speak of this body as the principal amid of sugar-cane.

In examining this sugar-cane amid to ascertain if it were optically active, solutions containing from two to four grams of the substance per 100 cc. of water were examined in a 200 mm. tube of a Schmidt and Haensch half-shade polariscope, observations being also made on similar solutions after the addition of caustic soda or nitric acid. In no case was any rotatory power shown. As asparagin is slightly left-handed in water-solution, more strongly so in alkaline solution and strongly right-handed in acid solution it was at once evident that the sugar-cane amid must be an inactive form of asparagin, or some other body not asparagin. A more extended examination soon brought out other points of difference between the sugar-cane amid and asparagin; and on comparison of the properties of this amid with those of the other known bodies, it was shown unmistakably to be glycocoll.

The chief points of difference between asparagin and the sugar-cane amid may be stated as below :

	Sugar-cane amid.	Asparagin.
Optical activity.	Inactive.	Left-handed in water solution.
Water of crystallization.	None.	One molecule lost at 100° C.
Behavior with Fehling's solution.	Does not reduce on boiling.	Reduces on boiling.
Behavior when boiled in alkaline solution.	Gives off NH_3 only if alkali is quite concentrated, leaving HCN in solution.	Gives off NH_3, leaving aspartic acid in solution.

It will be noted that these properties of the sugar-cane amid are identical with those of glycocoll, and in addition to this correspondence, both produce a gray precipitate of metallic mercury when added to a solution of mercurous nitrate, and both give a red coloration with ferric chloride.

The reaction by which the sugar-cane amid is most readily distinguished from asparagin, and by which also its identity with glycocoll is thoroughly established, is that which results on heating in alkaline solution. As is well known, asparagin gives off ammonia when heated in quite dilute alkaline solution, leaving aspartic acid in solution. On the other hand, glycocoll and the sugar-cane amid do not give off ammonia when heated in alkaline solution unless such solution be strongly alkaline, and after the evolution of ammonia has ceased no aspartic acid is found in the solution, but if hydrochloric acid be added to acidify and the solution heated, hydrocyanic acid is given off and can be detected by the smell, and oxalic acid is left in solution and can be precipitated as calcium oxalate. When operating with very small quantities of the amid, as I often found it necessary to do, the quantity of hydrocyanic acid given off in this reaction is so small that the smell is masked by that of the hydrochloric acid; in this case the presence of hydrocyanic acid can be established in the usual way by placing a drop of yellow ammonium sulphide on a porcelain dish, holding over the boiling solution for a few seconds, removing the excess of sulphide by blowing, and prov-

ing the presence of a thiocyanate by the red coloration produced on addition of ferric chloride.

The sugar-cane amid also gives off hydrocyanic acid when heated with dilute sulphuric acid and manganese dioxide.

When heated in a sealed tube with benzoic acid, the sugar cane amid gives hippuric acid, a condensation characteristic of glycocoll, and one by which it is supposed hippuric acid is formed in the animal body.

The hippuric acid so formed was identified by separating it from any remaining benzoic acid by agitation with petroleum ether, evaporating the insoluble residue to dryness with nitric acid and heating, when the characteristic smell of nitrobenzol was detected.

Glycocoll has been prepared in the usual way from hippuric acid by boiling with dilute sulphuric acid, and the reactions given above as characteristic of that body have been verified throughout.

It having been thus thoroughly established that the principal amid of sugar-cane is glycocoll, it is well to note that there are certain points in which glycocoll resembles asparagin, and the resemblance is such that anyone prone to jump at conclusions would on obtaining a crystallized preparation of the sugar-cane amid immediately pronounce it asparagin. The points of resemblance are these: first, the general appearance, solubility, etc., of the crystals; second, neither gives up any nitrogen when treated with sodium hypobromite in alkaline solution; third, both dissolve cupric hydroxide to a blue solution; and fourth, both contain the same per cent. of nitrogen. Asparagin crystallized with one molecule of water of crystallization and glycocoll each contain theoretically 18.66 per cent. nitrogen, while the average of all samples of the sugar-cane amid was 18.69 per cent. The Gunning method was used in determining the nitrogen, and clean, well-defined crystals were selected for such determinations.

In all, fifteen preparations of the glycocoll have been made from sugar-cane; and the samples of cane from which it has been prepared have included young shoots of cane a few weeks old, the green tops of cane one year old, and mature cane growing at elevations from 400 to 1,200 feet above sea-level. It is fair then

to conclude that glycocoll is not only the principal amid of sugar-cane, but is also a normal constituent of this plant at all periods of its growth.

I have as yet made no attempts to estimate the quantity of glycocoll in sugar-cane or any of its products, but have noticed that larger amounts have been obtained from young than from mature cane.

The average nitrogen content from mature sugar cane is probably about 0.30 per cent., and of this at least 0.22 per cent. is albuminoid nitrogen; so that the amido content cannot be higher than 0.08 per cent., and probably is often less than 0.02 per cent. It is easily seen then that the preparation of any quantity of the sugar-cane amid entails considerable labor, and this coupled with the fact that this work has been done at odd times during a busy grinding season, is my excuse for the incompleteness of this research in some respects.

The identification of glycocoll, glycocine, or amido acetic acid in sugar-cane is of interest from several points of view. Its occurrence has not been noted in a plant before, and it has been considered a body belonging wholly to animal chemistry. It can be prepared from gelatin by heating with acids or alkalies, in fact, was first prepared in this way, and it has been supposed that it was formed in the animal body from gelatin or gelatin-yielding proteids.

It does not seem to occur free in the animal body, and the theory of its formation from proteids seems to have been demanded by the following fact: Benzoic acid, when taken into the stomach, appears in the urine as hippuric acid, and to explain this it has been supposed that the condensation already referred to takes place; *viz.*, benzoic acid and amido acetic acid combine to form hippuric acid with the elimination of water.

$$C_6H_5COOH + CH_2NH_2COOH = C_6H_5CONHCH_2COOH + H_2O.$$

This view is strengthened by the fact that when glycocoll is taken with benzoic acid the yield of hippuric acid is increased.

In the urine of herbivorous animals hippuric acid occurs in relatively large quantities, and while the food of such animals has been deemed capable of supplying the benzoic acid part, the

source of the glycocoll to form such large quantities of hippuric acid has been more or less of a puzzle to physiologists.

The identification of glycocoll in sugar-cane and the fact that it has been mistaken for asparagin suggests the probability of its occurrence in other plants, especially the *Graminae*, which form the major part of the food of herbivorous animals; and it is quite likely that the source of the hippuric acid in the urine of such animals will be found in such occurrence.

In vegetable, as in animal physiology, the question of the constitution of proteids is uppermost. Now glycocoll in the physiology of sugar-cane no doubt plays the same part which other amids are known to do in other plants. It is the form in which nitrogen is conveyed to growing parts, and when maturity is reached the amid becomes the albuminoid to become the amid again when a new growth takes place. A number of facts collected during this study of the sugar-cane amid point to the existence in cane of a gelatin or gelatin-yielding proteid which yields glycocoll as one of the products of decomposition. This coupled with the well known and comparatively simple constitution of glycocoll seems a step toward the understanding of at least one proteid of sugar-cane. The further study of this matter promises to be of special interest, both from a physiological and a technical point of view.

From the sugar manufacturer's point of view the presence of glycocoll presents the following points of interest: It is known that at various stages of sugar manufacture ammonia is given off from boiling cane juice, especially if this juice has been rendered alkaline by an excess of lime. This has been stated as due to the decomposition of asparagin into aspartic acid and ammonia. But since we know that the amid is glycocoll and not asparagin, and that glycocoll is not decomposed unless boiled in strongly alkaline solution, it is plain that the ammonia must be derived from the decomposition of albuminoids. When, as is generally the case, cane juice is maintained approximately neutral throughout the course of manufacture, the whole of the glycocoll originally present in the juice should be found in the final molasses.

Whether this theory always carries out in practice, I have not yet ascertained, but I have obtained glycocoll in comparatively

large quantities from several samples of refuse molasses by the same method by which it was obtained from cane juice.

In one sample I determined the amounts of different forms of nitrogen according to a well known scheme of analysis with the following result :

	Per cent.
Nitrogen as free ammonia	0.011
Nitrogen as albuminoids	0.126
Nitrogen as peptones	0.050
Nitrogen as amids	0.201
Nitrogen as other forms	0.228
Total nitrogen	0.616

Free ammonia was determined by distilling with magnesia free from carbonate, and albuminoids by precipitating with cupric hydroxide. The nitrogen designated peptones is that precipitated by phosphotungstic acid after the removal of free ammonia and albuminoids. In the case of cane juice and its products this precipitate does not contain peptone bodies, and its character will be treated in a future paper. After removal of these three forms of nitrogen, amids were determined by boiling for an hour with two per cent. sulphuric acid, neutralizing and distilling with magnesia free from carbonate and doubling the amount of ammoniacal nitrogen obtained for amid nitrogen. This method which is fairly accurate in the case of asparagin which gives up half its nitrogen as ammonia when boiled with dilute acids, is of no value in the case of glycocoll, so that the above analysis should read amids and other forms 0.429 per cent. instead of

	Per cent.
Amids	0.201
Other forms	0.228

From a number of years' experience in working with cane juice, I am convinced that the formation of molasses is due to mechanical, rather than chemical, conditions, that the presence of viscous non-crystallizable bodies prevents the further crystallization of sugar by rendering the motion of the sugar molecules in the liquid difficult, and the mellassigenic action of crystallizable salts is very slight. A body such as glycocoll would then exert little effect on the crystallization of sugar one way or the other, especially as it exists in cane in such small

amounts, but it is likely that the proteid directly connected with glycocoll will be found to be highly melassigenic.

We have been in the habit of associating the so-called gums or viscous bodies in cane juice with the cellulose or non-nitrogenous constituents of the plant, but we may have to modify this view in the presence of a gelatin-yielding proteid peculiar to sugar-cane and allied plants.

LABORATORY OF KOHALA SUGAR CO.,
KOHALA, HAWAII, H. I.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE CASE SCHOOL OF APPLIED SCIENCE.]

XXIX.—THE INFLUENCE OF ANTISEPTICS ON THE DIGESTION OF BLOOD FIBRIN BY PEPSIN IN A HYDROCHLORIC ACID SOLUTION.[1]

BY CHARLES F. MABERY AND LEO GOLDSMITH.

Received September 27, 1897.

WHILE it may be difficult to perform experiments on artificial digestion under conditions that approximate those of natural digestion in the body, it is possible to determine the influence of substances that exert a retarding influence on the normal chemical reactions which involve the solution of fibrin or albumin by pepsin in an acid solution. The retardation by certain artificial colors, oroline yellow, saffoline, and magenta, was studied by Weber,[2] and the influence of alcohol in different proportions, and other bodies by Chittenden and Mendel.

In a recent number of this Journal,[3] Frank D. Simons gave an account of results which he had obtained in studying the action on the digestive ferments of salicylic acid, formol, several dyestuffs and essential oils.

In view of the stringent food laws that are everywhere recognized as necessary for the protection of the health and pecuniary interest of the consumer, the influence of adulterations commonly found in foodstuffs and in prepared foods should be well understood.

[1] The experiments described in this paper were made at my suggestion by Mr. Goldsmith, and they formed the subject of his thesis for the degree of Bachelor of Science. The paper was read at the meeting of the Cleveland Chemical Society, June, 1897. C. F. M.

[2] This Journal, **18**, 1092.

[3] *Ibid*, **19**, 744.

The results presented in this paper were obtained with alum, salicylic acid, boric acid, and formaline. The material used for digestion was blood fibrin separated by agitation in the ordinary way from fresh blood as soon as it was drawn from the steers. It was carefully separated into shreds as nearly as possible of uniform size and preserved in alcohol. For use it was thoroughly washed with water, spread out in thin layers on a glass plate, and dried at 100°. The digestive ferment was a scale pepsin, marked 1 : 3000, prepared by Armour & Co., of Chicago. In each of the following experiments twenty millimeters of pepsin was allowed to act in 100 cc. of a solution containing two-tenths of one per cent. of hydrochloric acid, on one gram of fibrin prepared as described above. The action was allowed to proceed for a definite time in a water-bath at 38°–40°, and the fibrin remaining after the experiment was stopped was removed by filtration, washed, dried at 100°, and weighed either on a Gooch filter or on a weighed paper filter. In every series of experiments the results were controlled by duplicate trials under the same conditions without the antiseptic.

EXPERIMENTS WITH ALUM.

First Series. Time 4 Hours.

Weight alum. Grams.	Weight undigested fibrin. Grams.	Per cent. digested fibrin.
0.00	0.0	100.00
0.00	0.0	100.00
0.01	0.0	100.00
0.01	0.0013	99.87
0.05	0.0132	98.68
0.05	0.0143	98.57
0.10	0.0150	98.50
0.10	0.0103	98.37
0.50	0.0979	90.21
0.50	0.0964	91.36
1.00	0.1196	89.04
1.00	0.1538	84.62
5.00	0.7017	29.83
5.00	0.7185	28.15

Second Series. Time 6 Hours.

0.00	0.00	100.00
0.00	0.0062	99.38
0.01	0.0102	98.98
0.01	0.0117	98.93
0.05	0.0155	98.45
0.05	0.0205	97.95
0.10	0.0162	98.38
0.10	0.0288	97.12
0.50	0.0600	94.00
0.50	0.0619	93.81
1.00	0.0813	91.87
1.00	0.0876	91.44

Third Series. Time 4 Hours.

0.00	0.0060	99.31
0.00	0.0070	99.30
0.00	0.0037	99.63
0.01	0.0103	98.97
0.01	0.0980	99.02
0.05	0.0235	97.65
0.05	0.0203	97.97
0.10	0.0349	96.51
0.10	0.0355	96.45
0.50	0.0798	92.02
0.50	0.0800	92.00
1.00	0.1780	82.40
1.00	0.1785	82.15
2.50	0.3472	65.28
2.50	0.3642	63.58

Fourth Series. Time 3 4-5 Hours.

0.00	0.0016	99.84
0.00	0.0025	99.75
0.00	0.0025	99.75
0.01	0.0031	99.69
0.01	0.0037	99.62
0.05	0.0070	99.30
0.05	0.0088	99.12
0.10	0.0247	99.53
0.10	0.0236	99.64
0.5	0.0810	97.90
0.5	0.0795	97.05
1.0	0.1797	91.03
1.0	0.1805	92.95
5.0	0.6094	82.06
5.0	0.6087	39.13

Fifth Series. Time 3 Hours.

0.0	0.0054	99.46
0.0	0.0063	99.37
0.02	0.0205	97.95
0.02	0.0192	98.02
0.10	0.0308	96.92
0.10	0.0345	96.55
0.20	0.0864	91.38
0.20	0.0755	92.45
1.00	0.7657	23.43
1.00	0.7540	24.60

In this last experiment equal weights of alum and sodium bicarbonate were used, and the weights are the weights of the mixtures.

The influence of the alum in retarding the digestive action of pepsin is clearly demonstrated by these results. Even with such small amounts as 0.01 gram, the influence is apparent, and it increases regularly and rapidly with larger proportions of alum. The duration of the experiment evidently affects the proportion of fibrin dissolved. In the fifth series the mixture of alum and sodium bicarbonate should reduce the acidity of the solution, thereby interfering with the normal condition of the digestive action.

For the purpose of testing the influence of alum under conditions of actual practice, two loaves of bread were prepared with the same weight of flour in each, one with alum baking powder containing alum, one part, sodium bicarbonate, one part, starch, one part; the other with a cream of tartar baking powder, composed of cream of tartar, two parts, sodium bicarbonate, one part, starch, one part. From the loaf after baking, the weight of alum was calculated. In each experiment sixty grams of bread were used, containing 0.75 gram of alum, or 1.5 grams cream of tartar, and in each trial the digestion was continued fifteen hours.

Kind of bread.	Weight bread undigested. Grams.	Weight bread digested. Per cent.
Alum	30.78	48.70
Alum	29.85	50.25
Cream of tartar	22.34	62.76
Cream of tartar	23.28	60.12

From these results it is evident that alum has an appreciable effect upon the proportion of bread digested.

A series of experiments was made to ascertain the effect of salicylic acid on the function of digestion. But on account of the small solubility of the acid, the action could not be tried with larger quantities than two-tenths gram of the acid. With this quantity an appreciable retardation is indicated. The proportions and conditions of the experiments were the same as those of the preceding experiments with alum.

Weight salicylic acid. Gram.	Weight undigested fibrin. Gram.	Digested fibrin. Per cent.
0.0	0.0276	97.23
0.0	0.0384	96.16
0.05	0.0484	95.16
0.05	0.0317	96.83
0.20	0.0671	92.29
0.20	0.0635	92.65

EXPERIMENTS WITH BORIC ACID.

Boric acid seems to exert an influence on the rate of change, but the proportion of acid does not seem to be essential. In the following series of experiments the times of filtration were somewhat irregular, and the first three tests which were intended as a means of control, were not altogether satisfactory :

Weight boric acid. Gram.	Weight undigested fibrin. Gram.	Digested fibrin. Per cent.
0.0	0.0393	96.07
0.0	0.0290	97.10
0.0	0.0155	98.45
0.05	0.0718	92.82
0.05	0.0754	92.46
0.10	0.0447	95.53
0.10	0.0504	94.46
0.30	0.0620	93.80
0.30	0.0380	96.20

EXPERIMENTS WITH FORMALINE.

The influence of formaline seems to be more marked than that of boric acid. In general the action is greater with the increase in weight of the antiseptic :

Weight formaline. Gram.	Weight undigested fibrin. Gram.	Digested fibrin. Per cent.
0.00	0.0393	96.07
0.00	0.0290	97.10
0.00	0.0155	98.45
0.05	0.0585	94.15
0.05	0.0413	95.87
0.10	0.0905	90.95
0.10	0.0752	92.48
0.30	0.1101	80.99
0.30	0.1045	89.55

While all the substances tested in these experiments show some influence on the digestive action of pepsin, only alum exhibits a marked effect. Although it is not possible, on account of the complex conditions existing in the stomach, to draw any conclusions from these results on what should take place in natural digestion, it would seem possible to conduct series of experiments on digestion within the stomach, introducing into the food suitable proportions of the antiseptics, and to determine the effects on the blood, and in other directions within the system. But such experiments are within the domain of physiological chemistry.

REVIEW.

SOME RECORDS OF RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.

During very recent years, progress in industrial chemistry, as in practically every field of human activity, has been peculiarly marked. Competition between manufacturers, depression in trade and commerce from various causes, the opening of new channels of consumption, have all done their share to establish that necessity, which from all time, has been such a vigorous stimulant to investigation and invention, and the results, as a rule, have been proportional to the needs presented. It is apparent in the advances being made that there is an increasing recognition of the value of rational over empirical work and of the effort of carefully educated men over that of men who, ignorant of the cardinal and fundamental principles of the processes they control, grope darkly after the ends they would attain. And so for us here, and at the present time one of the most important signs of progress is to be found in the increasing and exacting interest being manifested in all the leading manufacturing countries of the world in the education of technologists, and the im-

provement in means to that end. Germany and England have been particularly aroused regarding their special needs in this direction, and have been forced to it by the intense competition existing between the two countries in the different fields of industrial chemical activity. The education of technical chemists has therefore been the theme of discussion in the legislative halls, in the conventions of technologists and manufacturers, and in the meetings of the scientific and educational associations, and the feeling almost universally expressed is to the effect that the work of education should be made more thorough and exacting, and that it should be carried up from the technical high schools to the universities, and that the same care should be applied to technical instruction as is considered necessary in university work. So Dr. Böttinger, addressing the House of Delegates of Germany, urges upon the ministry the establishment of departments of technical chemistry with the necessary corps of instructors in the university and state examination of all technical chemists as soon as they shall have been graduated. Dr. Althoff, replying to Dr. Böttinger, calls attention to the extension of technical chemical work in the different institutions and particularly in the University of Berlin, and at the same time he calls attention to the more thorough study of physics, theoretical and applied, as it is particularly carried on in Göttingen. Dr. Lippmann declares that if progress in the chemical industries is to continue, the facilities for the education of technical chemists, (this class constituting ninety-five per cent. of the about 4,000 chemists in Germany), must be greatly improved. Similar ideas have been expressed by Professor Wichelhaus, Dr. Duisberg, Dr. Ostwald, and others of highest authority in both educational and technical fields. Dr. F. Fischer has treated the subject most exhaustively in a paper entitled "The Study of Technical Chemistry in the Universities and Technical High Schools of Germany and the Examination of Chemists."[1]

A congress, devoted to technical education, was held in London, June 17, 1897, the Duke of Devonshire presiding. In his opening address he compared the technical schools of England with those of other countries, extolling the organization and work of the technical schools of France and the Realschulen of Germany, and enlarged upon the value of thorough preparatory training of those who will enter the field of technical work with prospects of success. This Congress was likewise addressed by Dr. O. N. Witt, of Berlin, Dr. Lunge, of Zurich, and Dr. J. H. Gladstone, of London.

[1] The subject was further eloquently discussed in the general meeting, during the past summer, of the German Electro-Chemical Society, by Dr. Ostwald, Prof. v. Baeyer, Dr. Böttinger, Dr. Holtz, and others. The discussion is worthy of careful study.

Responding to the general demand, the new University of Brussels has established in the Gährungs Institut, under the direction of Dr. J. Effront, a summer course of study on subjects relating specially to the fermentation industries. It consists of lectures by eminent authorities in the different departments, accompanied by illustrative exercises in the laboratories for analytical chemistry, bacteriology, yeast culture and fermentation.

In our own country, while the demand is probably not so imminent, the possibilities of it have been most wisely foreseen by the directors of many of the educational institutions, and the extension of study to the applications of the principles of chemistry and physics is gratifying. In the East this is particularly manifest in the Massachusetts Institute of Technology, in Harvard University, Columbia University, Cornell University, and the University of Pennsylvania; and the institutions located west of the Alleghanies are working in the same direction with excellent results.

These are, it seems to me, the most important signs of fundamental progress in industrial chemistry that can be imagined or considered. We must all accept the expressed views regarding the better and more thorough education of the young men upon whom the responsibility for further progress must fall. For myself I have come to feel most acutely this necessity of our times and the desirability of a supply of young men who have had training not in the hurry of a year or two to make chemists who are analysts merely, and more frequently very indifferent analysts at that, but of those who have had the most careful training in the fundamental principles of the science, the physical relations of the elements and compounds, the thermal and electrical relations, the great theories upon which all productive practical work must be based. In many respects, heretofore, the tendency to specialization has been too marked and to the detriment of the all-round training necessary to effective work. Men carefully trained first in the fundamental principles and theories and then in the practice of observation and investigation are better able to apply themselves to specialties, than those trained as specialists are to meet the problems and difficulties which are likely to come to them in the conditions and situations in which they are sure, at one time or another, to find themselves. It seems to me, therefore, that the demand of the present time, and that of the immediate future, can be met only by broadly educated men; by men who have been trained not only in chemistry of itself, but in the great principles of physics as well. A good technical chemist must first of all be a good and thoroughly educated chemist; after that, to obtain the highest success in

this country, he must be educated in the principles of engineering; the production and applications of heat; the production and applications of electricity; the transmission of power; the movement of liquids; in general the means whereby the reactions of chemistry, which he may be called upon to apply, may be carried out in a large way. If the young men are to occupy commanding positions in the great chemical works, they must have preparation in these lines before they leave the educational institutions or they must acquire it after they have been graduated from them and have entered upon their life work. I agree with Dr. Duisberg, that whenever it is possible it is better to employ a chemist for chemical work, and an engineer for the engineering work in establishments where the best organization is to prevail, but in this country where the industries are in most cases not so largely developed as in Germany or England, and where beginnings have still to be made, the chemist will in very many cases be compelled to do his own engineering, even as in many cases the engineer must be his own chemist. We need, therefore, chemical engineers, and these in the nature of the requirements must be broadly and thoroughly educated men. While they must be trained for the work of the research laboratories, which are being organized in connection with many of the great industries, they must likewise be prepared to put into practical operation in a large way the results of the researches they have been called upon to make.

In this connection I cannot refrain from urging upon educators the importance of impressing upon young men that the controlling principle of successful work is the search for and establishment of truth; that honesty is after all the foundation of true progress; that absolute accuracy and personal responsibility are the prime necessities, and will be as firmly exacted in the valuation of a commercial product as it must be in the determination of an atomic weight.

It is not my purpose in this paper to enter further into the discussion of this great, interesting and absorbing question. I touch upon it by way of introduction, because of the great progress the present and continued agitation of it indicates, and the enormously important results which in the near future must flow from it.

Another important manifestation of progress in industrial chemistry is to be seen in the organization of the series of International Congresses of Applied Chemistry to be held once in two years in the different capitals of the world. The first of the series was held in Brussels in 1894, and the second was held in Paris last year. The latter was organized under the direction of the Association des Chimistes de Sucrerie et de Distillerie de

France et des Colonies, and met in Paris from July 27 to August 7, 1896, with over one thousand delegates in attendance from different countries, and nearly every branch of chemical industry represented. The several sections into which the congress was divided held more than sixty separate sessions, and it is stated that the report of the proceedings will require three volumes of at least 500 pages each.

One of the useful results of the work of the congress was the adoption of the proposition of the Verein Deutscher Chemiker, regarding the preparation and standardization of chemical measures. Two committees, one French, and another German, were appointed to consider this subject, and before the conclusion of their labors they are to meet together to prepare a report to be delivered and discussed in the next congress to be held in Vienna in 1898.

Most important results may be expected to flow from the labors of these eminent authorities, and the establishment of the committee illustrates most forcibly the demand for exactness and accuracy in technical work.

No less important as indications and records of industrial progress are the expositions of the products which are being held from time to time in different parts of the world. The Berlin Exposition held during the past year is an excellent illustration of this fact and the report of Dr. O. N. Witt upon it may be studied with profit by those who would gain a good knowledge of the progress of industrial chemistry in Germany as illustrated in the commercial products and manufacturing apparatus there exhibited. He describes the means for the use of liquid and pulverized fuel; the utilization of gas-house wastes for acid manufacture and as an accompaniment of this process the preliminary recovery of the ammonia and cyanides from the crude product; the production of material for the Welsbach mantles in which so great progress has been made during the past few years; compressed gases for various uses; the production of five chemicals; the persulphates and the admixture of these new and useful substances with the cyanides to be used in gold extraction; colors and organic disinfectants and remedies; fats and candles; soaps; artificial ethereal oils; and other substances of interest to chemists and of value to the industries. The information offered concerning the products exhibited and the principles upon which their preparation is based is extensive and the entire paper is characteristic of its author.

In like manner the report of Dr. Oppler on the department of chemical industries of the Bavarian Landesausstellung held in Nürnberg and opened May 14, 1896, is of most interesting value. The distribution of the exhibitors in this department is

an indication of the character of the information offered in the report of Dr. Oppler and the numbers in each class respectively are as follows: Salines, 4; heavy chemicals, 2; ordinary chemical preparations, 16; colors, 21; aniline colors, 1; explosives, 3; matches, 4; artificial fertilizers and glue, 17; resins and pitch, 6; soap-boiling and perfumery, 16; stearin and wax candles, 11; ethereal oils and petroleum distillates, 2; varnish lacquer and cements, 8; asphalt and roof covering, 2; rubber manufactures, 4; impregnating, 1; mineral water manufactures, 4.

That this exhibition should have been important was to be expected from the fact that in Bavaria, of a total population of 5,268,761, at least 685,298 are employed in the industries; that the Badische Anilin and Soda Fabrik in Ludwigshafen, which employed last year 4,800 persons including 100 educated chemists and 30 trained engineers, is to be included in the works represented. Besides the products of the truly chemical industries, metallurgical products, fuels and cements were largely represented and are exhaustively treated by Dr. Oppler in his report.[1]

The further register of the progress attained in the industries is to be found as well set forth in the literature of patents of invention as in other published matter. For it must be acknowledged that however much of careful work may be done in the research laboratories of the great industrial establishments or however important may be the immediate results of the application of new processes, the knowledge acquired finds its way to the published records but slowly and is generally held back because of the necessities of the active competition involved in the struggle for commercial supremacy. The protection afforded by the patent laws serves therefore a doubly useful purpose: that of preserving to the inventor or investigator the commercial results of his labor, and of bringing before the world without delay the truths which have been developed to serve as suggestion or incentive in further efforts in like or different directions. It will profit us therefore to consider briefly some of the developments which in this way the past year has brought forth.

It would be impossible in the time which could reasonably be allotted to such a paper to cover the entire field of industrial chemical activity and we must therefore be content with a limited scope. Some of the departments can be treated intelligently only by specialists working in them; and this applies particularly to the carbon compounds used as colors and dyes, as disinfectants and as remedial agents, the progress in the production of which has been enormous and most rapid. It is also true of the fermentation industries which have been so materially advanced by

[1] The exhibitions of Brussels and Leipzig have been very important and must have a marked influence upon all departments of industry and those involving the applications of chemistry must share the impulse. Valuable reports will doubtless be made of these two exhibitions.

biology and biochemistry; of the clay and cement industries which have been so much stimulated from the engineering sides. In metallurgy besides the further development of the basic process for manufacture of steel and the utilization of its wastes, the electrolytic production of aluminum, the electrolytic refining of the heavy metals as lead, copper, silver, and gold, considerable activity has been shown in the development of the cyanide and other processes for the extraction of gold from low grade ores by lixiviation. The cyanide process of MacArthur and Forrest has received special attention and has been improved by the addition of various agents to the solution for lixiviation to render it more active. Keith adds mercuric cyanide equal in weight to half that of the alkaline cyanide used and claims that the mixed cyanides act more rapidly and effectively than the alkaline cyanide alone. Mactear proposes the use of cyanuric acid equivalent to about five per cent. of the weight of potassium cyanide and to produce the compound within the solution by adding hypochlorite or hypobromite thereto. He claims that the solvent action of the cyanide is increased and that saving of cyanide is effected by reducing its action upon the base substances in the ore. The Chemische Fabrik auf Actien, recognizing that oxidation is necessary to the effective reaction between gold and the cyanide, and recognizing the disadvantages and losses attending the use of the metallic peroxides, permanganates, ferricyanides and hypochlorites because of their power to oxidize the cyanides to cyanates, have found that the persulphates, while they have no oxidizing action upon the cyanide even with considerable concentration and a temperature as high as 45° C. when mixed with the cyanides, render them peculiarly active as solvents for gold and silver. The solution is more active in the presence of free alkali which serves to combine with the acid liberated by the decomposition of the persulphate, and to form a compound which may be stored, transported and readily used, the company mix together ten parts of potash, forty parts of potassium persulphate and fifty parts of potassium cyanide. The mixture is dissolved in water in the usual way and in the usual proportions.

The same company have found that the nitro and nitroso-carbon compounds and the salts of their sulphonic acids have a similar intensifying influence upon the solvent power of the cyanides. For instance the addition of nitrobenzene to the cyanide solution is claimed to make it act from forty to fifty times as rapidly as the plain solution of equal strength.

For ores, to the treatment of which the cyanide process is not applicable, Lodge and Cassel and Hinman propose the use of weak solutions of bromine. A solution containing 0.15 to 0.25

per cent. of bromine is suggested and digestion of the ore with the solution is to be continued about two hours before final lixiviation. It is claimed that the solvent power of bromine is greater than that of chlorine and that it is further more effective because it carries less of baser metal into solution.

Endeavor in the separation of zinc from its ores and admixture with other metals has been active, and the results secured by Siemens and Halske seem to be of practical value. These authorities leach the ore containing zinc oxide with a solution of aluminum sulphate whereby basic aluminum sulphate is produced and zinc is carried into solution as the sulphate. The leach is electrolyzed when zinc is deposited at the cathode and the aluminum sulphate is regenerated at the anode. Kellner leaches the ore with a caustic solution, dissolving the oxide, obtaining a leach from which the metal may be extracted by well-known methods. And Mond modifies it by placing within the solution some sodium amalgam, plunging into the amalgam a rod of metal electronegative thereto, when the zinc is deposited on the rod.

Mond has further developed his process for the extraction of nickel dependent upon the production of the volatile carbonyl compound of the metal. In practice the metal is first reduced in the ore by means of hydrogen and the cooled ore transferred to the volatilizing chamber where, descending from one tray to another, it meets an ascending current of carbon monoxide gas. The carbonyl compound is carried to an adjoining chamber where decomposition takes place and the metal is deposited.

The example of Whitehead in the preparation of tellurium on a comparatively large scale has been followed by Farbaky in Schemnitz who has succeeded in obtaining an ingot of 820 grams of the purified product.

Hilbert and Frank have improved upon the production of phosphorus in that they avoid the intermediate preparation of the crude material by heating the latter in an electric furnace similar to that used for carbides. For instance ordinary calcium phosphate is ground up with carbon and the mixture heated in a properly constructed furnace. Reduction promptly occurs, calcium carbide is formed, and phosphorus and carbon monoxide liberated. Aluminum phosphate serves as well.

In the commercial production of the carbides some progress has been made. The production of the silicon compound, carborundum, is reported to have amounted in 1896 to 1,191,000 pounds of the crystalline variety. The amorphous product which accompanies the crystalline variety has thus far been of little or no commercial value but it has been suggested as a substitute for ferrosilicon in steel manufacture. It has been estimated that Ger-

many alone could use annually 2,500 tons of the product and an endeavor will be made to supply it.

The brilliant work of Moissan in the application of the electric furnace to the production of the carbides has brought forth among many others the titanium carbide which excels in hardness all known substances and which without great delay will probably become a commercial product.

The production and application of calcium carbide are extending. The Neuhausen Aluminum Company have established new works at Rheinfelden and the electro-chemical works at Bitterfeld have acquired land for the same purpose. The former company it is said will produce carbide at a cost below forty pfennigs per kilogram, a price scarcely encouraging. In spite of the extension of the manufacture comparatively little progress has been made in the process used beyond the mechanical appliances for making it continuous. The reduction in the cost of the product must be effected by reducing the cost of the power used.

What is true concerning the carbide is likewise true of the acetylene gas produced from it. Hundreds of devices have been made for liberating the gas for use in various ways all differing but little in principle and only as regards mechanical construction. Compared with coal gas and taking into account its illuminating capacity when used alone or mixed with air it is probably no more expensive but the prejudice prevailing regarding to sensitive character and the consequent danger attending its use in spite of the official reports regarding this quality will deter its wide application. Experiments with the gas in engines gave results unfavorable to its use in that way.

For use to enrich coal gas for illuminating, acetylene has proved less effective than benzene with which at the present time at least five per cent. of the gas used in Germany is improved. The declining cost of benzene due to its increasing recovery from coke-oven gases makes it available for this and many other uses from which, on account of cost, it has heretofore been excluded. It has been found particularly effective in the crude state when mixed with spirit for use in the incandescent spirit lamp. Experiment has shown that spirit mixture containing fifteen per cent. of xylene gives a temperature of 6,700° C. If the crude benzene in the spirit mixture be increased to $33\frac{1}{3}$ per cent. it is stated that it may be used as a substitute for petroleum in coal-oil lamps.

In Germany the process of extracting the benzene from the coke-oven gases has consisted in passing the latter through a tower against a finely divided stream of high boiling-point hydrocarbon oil and subsequently separating the benzene by fractional distillation, while the oil is cooled and returned to the tower. The quantity so produced up to the beginning of 1896 amounted

annually to from 4,500 to 6,000 tons and it is estimated that if the production should increase according to expectation it should reach as high as 80,000 tons.

Heinzerling proposes to recover benzene by compressing and cooling the gas and to this end the compressed gas is made to pass through a series of pipes which are cooled by a current of the gas from an expansion cylinder whereby a temperature of —70° to —80° C. is produced within the tubes. Two sets of condensing tubes are used alternately and the moisture and dust, which would seriously interfere with the process, are carefully removed. With a consumption of 240 horse-power produced from gas from the ovens 60,000 cubic meters of gas yielding 1,200 kilos of benzene are daily condensed.

Nikoforow has attempted to break up petroleum and its residues by repeated fractional distillation at temperatures ranging from 550° C. at ordinary pressures to 700° C. and even 1,200° C., with pressures up to two atmospheres, securing a yield of benzene equal to about twelve per cent. of the material used.

Mabery and Byerly convert petroleum residues into asphalt by passing a current of air through the heated mass. The distillation is begun at 450° C. and is continued until a temperature of 650° C. is attained. One of the products secured is said to be similar in its qualities to the natural product gilsonite.

In the desulphurization of petroleums Heussler proposes heating them with about five per cent. of aluminum chloride for twenty-four hours. At the end of the period, if the exhalation of gaseous products has ceased, the oil is distilled. Better results were obtained by doubling the quantity of the chloride and continuing the heating to 120 hours. Hinrici finds that equally good results may be obtained, with as great economy, by heating the crude oil with an equal weight of oil of vitriol of 66° B. With crude oil containing one and two-tenths per cent. sulphur he obtained a solar oil distillate containing 0.063 per cent. of sulphur. At this rate he finds the acid no more expensive than the chloride and equally effective.

Many of us will remember that somewhat more than a year ago, Nikodem Caro published the results of his experiments in the preparation of alcohol from actylene after the reactions established by Berthelot, obtaining a yield so far below what theory requires, as to render the reaction a practically hopeless one. The production of synthetic alcohol has been revived by Fritsche who has made use of the reaction discovered by Faraday and subsequently studied by Berthelot to whom it has often been credited. Attempts had been made successively by Berthelot, Cattelle and Mallet, to extract the ethylene from coal-gas and convert it into alcohol but all failed because of the presence of other

substances which were extracted at the same time and interfered with the subsequent reactions. But since the establishment of the coke-ovens and the extraction of the tar, ammonia, and benzene so completely from the gas Fritsche concluded that the ethylene could be profitably recovered and utilized. The eighteen coking establishments of Germany using a million and a half tons of coal, yielding gas containing one to one and eight-tenths per cent. of its volume of ethylene should represent an annual possible production of 95,000 hectoliters, (nearly 2,500,000 gallons) of alcohol. The large number of experiments made showed that complete absorption of ethylene may be effected by strong sulphuric acid, and when the acid is kept at 140° C. the absorption is very rapid and may be carried to a concentration of 50 per cent. of the compound produced without exhausting the absorbing power, so that 100 pounds of vitriol will serve for the absorption of 14 kilos of ethylene which will yield 18 kilos of alcohol. For the production of 100 kilos of alcohol, 350 kilos of 66° B. sulphuric acid will be required and for the complete recovery of the alcohol this must be mixed with at least 500 liters of water. The water is subsequently evaporated and the acid recovered.

Fritsche expresses doubt if, at the present cost of alcohol, the process, which gives yields very close to theory, may become profitable. But for the production of such alcohol derivatives as potassium ethyl-sulphate, ether and acetic ether, etc., he considers it has some possibilities.[1]

In the manufacture of the acids and the bleaching compounds some advances have been made, but in this department of industry progress is necessarily slow. Attempts have been made to replace the lead chambers in vitriol manufacture by stoneware towers, but thus far the adoption of the improvements claimed has not been extensive. The demands of the color and explosives manufacturers for pure nitric acid of high concentration have naturally stimulated endeavor to meet them and with good results. Dr. Hart's condenser with its return connections has already found very extensive application and has proven most effective in yielding a high grade and pure product. Dieterle and Rohrmann endeavor to attain the same end by passing a current of air into the distilling chamber and providing return connections in the condensing coils to a side pipe for the escape of the air carrying the halogen and other impurities. The nitrous compounds are said to be oxidized to nitric acid and the high grade distillate to be therefore free from these troublesome substances. Dreyfus decomposes alkali nitrates at a temperature carefully regulated at 170° to 190° C. in a vessel in which a vacuum may

[1] Fritsche has since patented a process for manufacture of ether from ethylene and claims that practically theoretical results may be obtained.

be maintained. Main and Stevenson heat a nitrate and manganese dioxide together in a muffle and convey the nitrous compounds liberated to an oxidizing tower fed with dilute nitric acid. The nitric acid produced is finally distilled from strong sulphuric acid, yielding a product of high degree and the sulphuric acid is concentrated by evaporation for use in subsequent charges. The residue in the muffle is heated with steam, and sodium hydroxide and manganese dioxide recovered.

Valentiner recovers the nitric acid from waste acids by distilling it from strong sulphuric acid in a vacuum. He states that if a mixture of 800 kilos of strong sulphuric acid and 1,200 kilos of impure nitric acid of 1.40 sp. gr. be distilled *in vacuo* so that the temperature may not exceed 100° C., all the water and impurities will be held back and nitric acid of 94 to 96 per cent. of monohydrate will be obtained.

The Verein Chemischer Fabriken likewise distil the acid from strong vitriol. From a properly constructed vessel containing sulphuric acid the nitric acid vapors are carried into a tower fed with water heated to 85° C. and from here they pass to the cooling condenser. The warm water absorbs the impurities and returns them to the still and the pure acid issuing from the condenser is said to have a strength of at least 94°.

Jung and Steuer undertake to recover hydrochloric acid by a somewhat round-about process from the calcium chloride of the ammonia soda process. The properly concentrated chloride liquor is mixed with copper sulphate to produce double decomposition. The cupric chloride separated from the calcium sulphate is decomposed by hydrogen sulphide. The copper sulphide separated from the hydrochloric acid is exposed to the air in thin layers to be oxidized to sulphate for subsequent use in the process while the calcium sulphate is heated with carbon, in furnaces, to reduce it to sulphide, which, in turn, may be treated for sulphur by the Chance process. It is extremely questionable if the hydrochloric acid can be obtained in this way entirely free from lime salts, but the inventors suggest that these will not interfere particularly when the acid is to be used for the generation of chlorine by the Weldon process.

In view of the rapid extension of the production of chlorine by electrolysis, the reaction, occurring when aqueous vapor and chlorine are led over glowing carbon, producing hydrochloric acid and carbon monoxide, acquires a higher interest. It is possible that the process based upon this reaction may yet prove profitable, and certainly it will be free from the growing objection of the old process, that it will leave behind no residue of cumbersome sodium salts.

In the generation of chlorine from hydrochloric acid, a great

deal of experiment and investigation have been carried on. The improvement of the Deacon process by passing air along with the acid gas, Mond's substitution of nickel for the copper of the Deacon process, and the various modifications of the reaction between nitric acid and hydrochloric acid have all had their supporters. The latter reaction has had the largest share of attention, but in spite of all the thought and energy which seem to have been devoted to it, the promise for its future is not brilliant. All the processes and forms of apparatus devised for carrying out the reaction depend upon bringing the nitrosyl chloride into proper contact with vitriol. The process and apparatus seem to have the merit of greater simplicity, at least, than the others described, and the essential part thereof consists in perfecting the oxidation of the hydrochloric acid and the decomposition and removal of the nitrous compounds by systematically subjecting the gas alternately to the action of nitric acid and hot sulphuric acid. To effect this they arrange two vertical towers, each divided into compartments by diaphragms with hydraulic seals. A stream of nitric acid is made to flow downward through one tower and hot sulphuric acid to descend through the other. Gas from the decomposing apparatus and containing nitrous compounds is introduced to the bottom of the lower compartment of the nitric acid tower and passes from the top of this to the bottom of the lower compartment of the vitriol tower. From the top of this, in turn, the gas passes to the bottom of the next upper compartment of the nitric acid tower, then from the upper part of this compartment back to the bottom of the second compartment of the vitriol towers and so by zigzag course from one to the other, until it finally passes out from the top of the vitriol tower dry and free from hydrochloric acid and nitrous compounds. The acids used in the towers are regenerated for use in subsequent charges.

As before stated, this differs practically only in the mechanical arrangement for effecting the oxidation and the purification of the chlorine gas, and is therefore similar to the processes of the Wallis chlorine syndicate, of Sadter and Wilson, Scott and Vogt, Verein Chemische Fabriken zu Mannheim, Krause, and others, which have been described within the past year and a half. The complicated character of the apparatus required, the difficulty in moving the corrosive gas, the losses of nitric acid, all conspire against the extensive application of any of these processes in competition with the new electrolytic processes for the same purpose. The latter are being adopted with enormous rapidity, as may be gathered from some statistics from Germany for 1895 and 1896. Thus, from January 1 to the end of September, 1896, the imports of chloride of lime were 3,342 tons, and the exports 50,549 tons; while for the corresponding

period of 1895 the imports were 10,232 tons, and the exports 23,636 tons. In Austria, it is stated, that works using 200 horse power are in operation, and those requiring 3,000 horse power in process of erection. In England these processes have been received with peculiar favor and thousands of horse power are being consumed in the works devoted to them. At Saltville, Va., the Matthieson Alkali Company have made a beginning and have projected works to be erected at Niagara Falls covering twenty acres of ground. These works, when completed, will use the Castner process, and employ 150 men and 2,000 horse power.

The methods which have been found most effective and acceptable are those without diaphragms, like that of Castner and Kellner, and those with diaphragms similar to that of Hargreaves and Bird. Thus far the former have had the widest application, although it is claimed that the Hargreaves cell can be operated with a lower consumption of power. The difficulties in the operation of both kinds are, however, being rapidly overcome, and we are likely, in the near future, to be called upon to record the entire replacement of the old chlorine and soda plants by those operating the electrolytic processes.

Before leaving the subject of electrolysis in the production of bleaching compounds, we may not overlook the new and interesting peroxidized substances—persulphates and percarbonates—which bid fair to replace many of the well-known oxidizing and bleaching agents.

Persulphuric acid and the persulphates are produced by the electrolysis, respectively, of the free acid or the acid salts. The most useful, however, are the potassium, ammonium, and aluminum salts, that of ammonium being the most stable. In like manner Constam and von Hansen produce the potassium percarbonate by electrolyzing a saturated solution of potassium carbonate, kept at a temperature of —10° to —15° C. Platinum electrodes are used in a cell with a diaphragm and the product obtained, which decomposes readily, must be protected from heat and dried quickly. It is comparatively stable in iced water, but in warm water it breaks up with production of free oxygen. Both classes of salts may be used as oxidizing agents, and the persulphates, as already stated, have been recommended for use in the cyanide gold extraction process, to intensify the solvent action of the cyanide solution.

Wolffenstein finds that hydrogen peroxide solution, if free from certain impurities, may be concentrated by ordinary evaporation to about fifty per cent. To concentrate it further it may be extracted with a substance, like ether, insoluble in water. After removal of ether the product may be distilled in a vacuum

of sixty-eight mm. and a temperature of 84°–85° C., yielding a distillate containing ninety-nine per cent. of the peroxide.

It is probably true that in no field of chemical industry has greater activity been manifested than in the production of the compounds of nitrogen, and particularly ammonia and the cyanides. The increasing demands of agriculture, the manufacture of the various nitro compounds for colors and explosives, and the new gold extraction processes, have long served to stimulate the search for new sources of combined nitrogen and the effort expended is beginning to bear fruit. Heretofore, the principal known sources of combined nitrogen have been animal or other organic matters, and coal and the niter beds of South America. The latter has been an almost constant source of supply. That from animal matter has grown with the growth of the great meat-packing industries and the recovery of their waste products, while the improvements continually being made in the gas and coking industries would seem of themselves almost capable of meeting the demands. It is interesting in this connection to compare the English statistics for sulphate of ammonia production in 1886 and 1895, respectively.

	1886. Tons.	1895. Tons.
Gas works	82,480	119,645
Shale works	18,090	38,335
Iron works	3,950	14,588
Coke works	2,100	7,083

The iron works ammonia is produced largely in Scotland, where, it is stated, as much as two and a quarter million dollars are invested in its recovery.

Hagenstock, of Dalhausen, states that Rhenish Westphalia alone produces annually 6,000,000 tons of coke, using 8,000,000 tons of coal. On the basis of the recovery of ammonium sulphate, equal to one per cent. the weight of the coal, the amount annually recovered should be 80,000 tons, worth $4,000,000. Knublauch gives some interesting figures regarding the distribution of nitrogen in the distillation of coal and finds that about fifty per cent. of the nitrogen remains in the coke, thirty per cent. remains in the gas, twelve to fourteen per cent. is converted into ammonia (corresponding with 10.55 pounds sulphate of ammonia per ton), nearly two per cent. into hydrocyanic acid (equivalent to 1.42 pounds ferrocyanide per ton), while one and a half per cent. is found in the nitrogen bases in the tar. On the basis of a yield of 0.20 to 0.25 per cent. of the weight of the coal, the 1,000,000 of coal, which he estimates is daily consumed in the gas-works and coke-ovens in the world, the sulphate available should amount to 10,000 to 12,000 tons. Yet Truchot, quoting Legrand, declares that Belgium uses in agriculture but

one-sixth, Germany one thirty-sixth, France one fifty-fourth, and England one sixty-sixth the nitrogenous manures they might use with advantage. If this estimate of Legrand be correct it is easy to see that the possible demand is far from being met at the present time.

The indirect utilization of atmospheric nitrogen by vegetation has now been fully established. Von Beyerrinck, Hellriegel, Wilfarth, Nobbe, and others, find the most important agent in this connection to be the bacteria of the root nodules of leguminous plants. And Nobbe and Heltner find that these nitrogen-fixing bacteria, when introduced to soils free from them and unsuited to the cultivation of leguminous plants, produce in the roots of such plants nodules or tubercules, in which fixation of free nitrogen and its conversion into assimilable forms is effected. Soil wanting in assimilable nitrogen, and therefore practically sterile, becomes fruitful and will produce good leguminous crops when inoculated with the bacteria.

The bacteria are produced in agar gelatine containing sugar and asparagin or the green substance of the plant. The culture medium, when saturated, may be dissolved in water and so be used to moisten the seed, or it may be mixed with dry earth, which is sown broadcast. The firm of Meister, Lucius & Bruning, in Höchst on the Main, have undertaken to produce cultures of the bacteria commercially and supply them in form convenient for transportation, preservation, and distribution. The cultures are enclosed and marketed in small bottles, each containing sufficient to inoculate half an acre of ground. The success of the new industry remains to be established.

In the production of ammonia from sources other than those mentioned, Sternberg proposes the ignition of such organic matters as sugar-house waste, with alkali aluminate made by melting together lime, crude potash, and bauxite or clay. This, finely ground, is mixed with the organic waste, such as molasses, and charged to the top of a vertical retort so arranged that the gases generated may be drawn over the hotter charge at the bottom. From time to time the aluminate is drawn off at the bottom to be used again, and fresh material is charged to the retort at the top. Nitrogenous gases may likewise be passed over the hot material for ammonia production. This process has elsewhere been credited to F. O. Matthieson.

Raschen and Brock propose passing a mixture of nitrosyl chloride and hydrogen over heated platinized asbestos whereby, in presence of some excess of hydrogen, reduction is effected and ammonium chloride is produced. The vapor is conducted into a chamber maintained at 100° C., where the salt is deposited. In like manner it is stated that nitrogen oxides may be reduced to ammonia.

Lord Rayleigh has lately made a study of the oxidation of free nitrogen under the influence of the electric spark. He made a large number of experiments and obtained the best results by confining in a flask a mixture of eleven parts of pure oxygen and nine parts of air, passing through the mixture a spark from a current of forty amperes and 8,000 volts. In practice he forced a solution of potash into the flask in such a way that its walls were constantly washed, the liquor being kept cool, and passed the mixed gases through the flask while the current was in operation. His results showed the efficiency to be equal to twenty-five cc. of absorption per Watt hour.

Following the same line of thought, Siemens and Halske claim that when air or oxygen and nitrogen are mixed with ammonia and subjected to the influence of the silent electrical discharge a profitable yield of ammonium nitrate may be obtained. It is important to the efficiency of the reaction that the air or gases and the ammonia shall be perfectly dry before they enter the apparatus, and that the air be previously ozonized. In practice the dried air and ammonia gas in proper proportions, which are found to be one volume of air and 0.01 to 0.02 volume of ammonia are passed slowly through an apparatus similar to that for producing ozone, and it is claimed that if the precautions described are carefully observed, the whole of the ammonia will be converted into ammonium nitrate. From the results obtained by Lord Rayleigh and by Siemens and Halske, it would seem that the presence of an alkaline substance to combine with the oxides at the instant of their formation is necessary to the reaction.

Since the discovery of argon and the application of magnesium and lithium to the removal of the nitrogen from the deoxidized air by the formation of the nitrides, considerable attention has been devoted to the commercial production of these interesting compounds. Rossel and Franck studied the subject experimentally following the suggestion of Winkler that the combination of magnesium and nitrogen is favored by the presence of an indifferent substance to prevent oxidation, heat together at red heat in an open crucible, a mixture of calcium carbide and magnesium powder, and find that the magnesium is practically all converted to nitride. They state further that under similar conditions aluminum, zinc, and iron will take up nitrogen.

Mehner, and likewise Willson, following the same idea, expose such elements as boron, silicon, magnesium, and titanium as are capable of combining with nitrogen at high temperatures, to the heat of an electric furnace in presence of carbon and nitrogen, using a current of high tension. Franck obtained aluminum nitride by heating the finely divided metal with powdered calcium carbide in a crucible and declares that when the metal is

heated with dry slaked lime the nitride may be obtained in large quantity. Practically all the nitrides yield ammonia when mixed with water. In the cold the aluminum compound decomposes but slowly, and Franck suggests that on this account it may have considerable manurial value. The production of nitrides in the electric furnace by the methods of Mehner and of Willson may become profitable sources of ammonia.

Experiment in the production of cyanides has been particularly active and practical advances have been made toward the acquirement of sources heretofore unavailable. In the old method of fusing nitrogenous organic matter with alkalies and iron, comparatively little improvement has been made. Bower adds iron thiocyanate to the melt toward the end of the operation and claims to secure thereby an increased yield. Reichard and Bueb submit lyes and molasses to dry distillation and slowly pass the gases generated through flues heated to 1,000° to 1,100° C. The gases finally pass through an absorber charged with a solution of iron salts. For such absorption Holmes recommends the use of an alkaline liquid in which ferrous carbonate is suspended. Drehschmidt recommends a mixture obtained by decomposition of a ferrous salt with calcium or magnesium carbonate and declares that this mixture is particularly favorable to the extraction of the cyanides from illuminating and coke-oven gases when much carbon dioxide and hydrogen sulphide are present. From the gas of coke-ovens the quantity of cyanides to be obtained is said to be variable according to the temperature of the oven. Thus a published report states that with a temperature of 900° C. eight grams of sodium ferrocyanide was obtained from a cubic meter of gas, while with a temperature of 950° C. the yield was increased to fifty-six to ninety-five grams of the salt.

Aitken proposes special construction and operation of blast furnaces with a view to the production and recovery of cyanogen. Two stacks erected alongside each other and rather higher than usual are connected by a lateral tube or pipe at the top. When the blast has been shut off from one and the slag and metal are being drawn off, a draft is started through an opening near the tuyeres and gases from the second furnace, drawn downward through the heated charge of the first. When the charge has finally been drawn off, the draft is stopped and the blast started again. When the second furnace is being tapped, the draft is made from a similar opening near the tuyeres and gases from the first furnace drawn downward through the charge of the second. In this way the furnaces are operated alternately and the gases drawn off are said to be particularly rich in cyanogen.

Nikodem Caro, in *Die Chemische Industrie*, and Conroy, in a paper presented to the Society of Chemical Industry, of England, have discussed the production of cyanides in a most interesting and instructive manner, the former from a more or less theoretical standpoint and the second from the results of a series of critical experiments made for the United Alkali Company. Both of these papers are full of practical suggestion and well worth careful study by every one interested in this branch of chemical industry. Naturally, both these authorities classify the methods used and available, as follows: (1) those producing cyanides directly and involving the use of atmospheric or other nitrogen and heat, and (2) wet methods with intermediate production of the thiocyanates. Neither, however, recognize the methods involving the reduction of oxidized nitrogen compounds. Under the first class Caro discusses the history of the reaction, and the work of Liebig, Karmrodt, Beilby, Barr and MacFarland, Siepermann, and others, in which, in various ways ammonia gas is brought into contact with carbon, impregnated with potash. Karmrodt obtained a yield of only about twenty per cent. of the theoretical. Beilby hoped to improve upon it by adding to the carbon-alkali mixture twenty per cent. of potassium cyanide, whereby it could be kept fluid, allowing the mass to flow over gratings arranged in a vertical column, while the ammonia gas was passed upward through the same column. Barr and MacFarland considered cyanide to be formed by double decomposition of carbon monoxide and ammonia, and Siepermann proved that the reaction between potassium carbonate and ammonia was possible without the intervention of carbon forming cyanate, potash, and water. To avoid the subsequent reduction of the cyanate with carbon he proposed mixing the potassium carbonate with barium carbonate and carbon, making a single operation of the reactions, and Caro declares that experience with the process shows it to be perfectly operative.

Conroy, discussing these reactions from the standpoint of his own experiments, states that operating with the process of Grüneberg, absorbing the ammonia at a low temperature and reducing the resulting cyanate at a higher temperature with carbon, he obtained a yield of only four per cent. of the ammonia entering the apparatus. With the process of Young and MacFarland, heating in a bent tube to 1,000° to 1,200° C. caustic potash and carbon in the proportion of 10 : 1 by weight, adding powdered charcoal from time to time till the weight added reached twenty to thirty per cent. of the weight of the potash used, he passed through the molten mass a carefully dried mixture of nitrogen, carbon monoxide, and ammonia, and secured a conversion to cyanide of thirty to thirty-three per cent. of the ammonia used. Time seemed to be an important element in the

reaction and production seemed to increase with the proportion of cyanide present.

Caro, discussing the methods involving the use of free nitrogen and heat, offers an extended review of the history of the reaction and process depending upon it from its discovery by Bunsen and Playfair to the present, and accepts Berthelot's explanation of the reaction that it depends upon the formation of potassium carbide, which in the heated condition may combine with nitrogen to form potassium cyanide. This, he considers, would satisfy the conditions of the process of Lambilly which, he says, consists in heating a mixture of potassium, sodium or barium carbonates with carbon as long as carbon monoxide is evolved and passing over the resulting mass at white heat, equal parts of nitrogen and illuminating gas, under pressure corresponding with ten to fifteen cm. of mercury. But Lambilly subsequently modified his process by first producing pure acetylene and passing this in admixture with pure atmospheric nitrogen over the hot alkali and carbon. Again, in the application of the Fogarty process in Pittsburg, whereby a mixture of finely divided lime and coke were fed into the top of a narrow vertical furnace provided with baffling plates and heated from the top to a temperature of 2,200° F. by the products of the imperfect combustion of a natural gas, cyanides were produced under conditions favoring the production of acetylene and its subsequent contact with heated alkali and carbon. A question naturally arises as to the possible part of acetylene in this reaction.

Both Caro and Conroy seem to consider the wet method of Gelis and its modifications to be the most promising. This, it will be remembered, consists in heating together ammonia and carbon disulphide, converting the ammonium thiocyanate into the corresponding calcium salt and this, in turn, by means of potassium sulphate into the potassium salt, which may then be desulphurized with iron. The process is said to be carried out by Grolich and Wichmann, in Hamburg, but the desulphurization by iron is found to be satisfactory only when filings are used in double the theoretical quantity and the whole heated under pressure to 110° to 120° C., whereby 80 per cent. of the theoretical yield is obtained.

Conroy, like others, found the consumption of ammonia, due to the production of sulphide, to be inconveniently high, and the pressure resulting from the production of hydrogen sulphide to be troublesome. He favors the suggestion of Hood and Salomon that manganese dioxide alone, or mixed with lime, be added to the charge, whereby their cyanides and sulphides are produced, leaving all the ammonia available for conversion into cyanide. Operating under the suggestions of Crowther and Ros-

siter, and of Hurter and Hethrington, Conroy heated together in a properly constructed jacketed vessel slaked lime, water, ammonia, and carbon disulphide, agitating the mixture and keeping it at a temperature of 100° C. for two hours. The thiocyanate remains in solution after distilling off the excess of ammonia and precipitating the lime with carbon dioxide. Conroy obtained quantitative results with this method.

From the results of his experiments he concludes:

1. "That the reaction between carbon disulphide and ammonia to form thiocyanate proceeds easily and completely. The addition of lime does not influence the yield one way or another, provided ammonia is present in excess, but simply serves to reduce the pressure within the apparatus.

2. "That carbon disulphide and calcium sulphide combine quantitatively in theoretical quantities when treated under suitable conditions to form soluble thiocarbonate. The combination takes place in the cold or at 100° C., but especially well at 50° to 60° C.

3. "That the solution of calcium thiocarbonate may be quantitatively converted under suitable conditions into thiocyanate. For good yield, large excess of ammonia must be present."

It has been proposed to replace part of the lime by magnesia, which under pressure absorbs hydrogen sulphide, evolving the gas below 100° C., or release of the pressure, while the base is precipitated for reuse.

For desulphurization of the thiocyanate Conroy favors the use of iron. To secure a good reaction (1) the material must be perfectly dry, (2) the iron must be finely divided, (3) the substance must be intimately mixed, and (4) a reducing atmosphere must surround the reacting mass.

Since the publication of these papers of Caro and Conroy, many interesting developments in the production of cyanides have been made, modifying or extending the old processes or introducing new ones. Troyman passes the gases issuing from the Bessemer converter between the cooling period and the drop of the flame into a basic-lined chamber filled with coke saturated with alkali carbonate, and recovers the cyanide by subsequently leaching the coke. Swan and Kendal mix carbon and tungsten, or saturate charcoal with potassium tungstate, heat the mixture in a properly protected tube of nickel or iron, cause a current of fused potassium carbonate to flow through the tube along with free nitrogen or ammonia, collecting the resulting cyanide in a suitable receiver at the lower end of the tube. Rad and Rosenfels heat such carbides as barium and calcium in a current of nitrogen or ammonia gas and get better results when the carbides are mixed with alkali carbonates. When ammonia is

used, hydrogen is liberated. Caro and Frank find that cyanogen compounds are formed when nitrogen and aqueous vapor are passed over carbides heated to dark redness in closed vessels. In practice they charge finely divided barium carbide into a tube-shaped retort, provided with inlet and outlet for gases and vapors. Nitrogen gas saturated with moisture is passed through the retort, and at the end of two hours the reaction is complete and the charge is withdrawn. They subsequently modified their process by passing ammonia gas over the heated carbides, forming alkaline cyanide and free hydrogen.

Pflege has made the interesting discovery that the absolute exclusion of oxygen is not necessary to cyanide formation. He uses a flat, covered, magnesia-lined furnace, whose sole is covered with a mixture of carbon and alkali in thin layer, and through which air may freely circulate. The space in the furnace above the charge and under the cover is proportioned to the quantity of air needed for local combustion. The furnace is so heated from below that the carbon may become ignited in contact with air, and during the resulting combustion cyanide production is said to proceed rapidly and with very high yield. The reaction is completed at the end of three hours. He modifies his process by placing 1,000 parts of potash and 100 parts of carbon in a crucible and heating the mass to 900° C., producing fusion. Then through a tube passing through the cover and projecting into the mass, he introduces a rapid stream of ammonia. As the carbon is consumed an additional quantity is blown in with the ammonia. At the end of three hours the alkali should all be converted into pure cyanide without by-products or impurities.

Bergmann, by passing a mixture of ammonia and coal-gas over carbon heated to 1,180° C., obtained conversion of sixty per cent. of the ammonia to cyanogen. One-half the residual ammonia was recovered and the remainder split up. Exclusion of oxygen seemed favorable to the reaction.

With all the manifold uses of the electric furnace it is natural that it should be applied to the production of the cyanides. Willson heats a metal or metalloid together with carbon in the electric furnace and subjects the heated mass to a current of nitrogen or producer gas, forming nitrides and cyanides, or the gases are passed through heated carbides in a separate furnace. Readman heats the oxides or carbonates of the alkali metals together with iron and carbon in an upright furnace with an electrode at the top and bottom and passes nitrogen or generator gases over the incandescent mass, collecting the fused cyanide or ferrocyanide at the bottom. Horning generates metallic vapors in the electric furnace and mixes them with carbon or

carbon compounds, preferably hydrocarbon gas or vapor and nitrogen, using considerable excess of the carbon and nitrogen. Mehner charges a U-shaped furnace with carbon and a fusible cyanide such as the barium compound and electrolyzes the mass, liberating cyanogen gas at the positive pole and barium at the negative pole. Generator gas is passed through the mass during the operation, the nitrogen combining with the carbon to form cyanogen which in turn combines with barium and is ultimately liberated at the anode. Blackmore prepares iron carbide in the electrical furnace, pulverizes the product, suspends it in a bath of fused alkali sulphide and passes nitrogen through the fused mass.

Castner makes use of the reaction between sodium and ammonia forming sodium amide and that between sodium amide and carbon producing the cyanide. His process is carried out in two operations in different apparatus. Sodium is fused and charged to a properly constructed retort from which air is excluded and heated to 300° to 400° C. Thoroughly dried ammonia gas is passed into the retort and the amide formed is conveyed to a second vertical retort which is charged with carbon and heated to dark redness. The amide dropping upon the carbon is converted into cyanide with the liberation of hydrogen and the resulting cyanide is drawn off from the bottom of the retort in a fused condition.

Moïse utilizes boron nitride formed by heating borax in vapor of ammonium chloride for the production of cyanide. The compound mixed with carbon and potassium carbonate is heated to red heat in a crucible for about an hour. The resulting mass, consisting of potassium borate and potassium cyanide, is leached with alcohol dissolving the cyanide, leaving the borate for reuse.

Finlay mixes equal parts of carbon and alkali or alkaline earth (preferably barium carbonate), heats the mixture in a retort to 1,000° C., and subjects it at this temperature to a current of nitrogen and sulphur dioxide gases. When sufficient barium cyanide has been formed, the mass is pulverized, the barium cyanide and thiocyanate leached out, the leach decomposed with carbon dioxide and the cyanogen liberated collected in a soda solution. The barium carbonate is used in a succeeding charge.

Kerp has observed that when sodium acetate and sodium nitrite are fused together sodium cyanide is produced and that though in his experiment decided quantities of cyanogen gas escaped, the amount obtained was more than twenty-five per cent. of the theoretical yield.

Kellner found that when a nitrate or nitrite is subjected, either alone or mixed with nitrogen-free carbon, to the action of an arc between carbon electrodes of an electric furnace, cyanides

are produced, and Huntington has patented a process in which a mixture of acetylene and nitrous oxide in about equal volumes are drawn into the cylinder of a gas engine and exploded with a spark. The products of the explosion consisting of carbon monoxide, hydrogen, and cyanogen are passed through an alkaline solution whereby the cyanogen is absorbed and the other gases are allowed to pass along to be used as fuel.

Hood and Salomon produce thiocyanates by heating together caustic soda, carbon disulphide and ammonia, and desulphurize the resulting compound with lead or zinc. They find further that for the production of cyanogen compounds carbon disulphide may be replaced by carbon dioxide. In utilizing this principle, which seems opposed to past experience in this branch of chemical industry, they mix alkaline carbonate with finely divided zinc or manganese, heat the mass in a retort provided with a stirring gear and pass over the heated mass a current of ammonia gas. If sodium carbonate and zinc are used the products of the reaction are sodium cyanide, sodium hydroxide, zinc oxide, and water. It is recommended that a small quantity of carbon be added to the mixture to increase the yield of cyanide. The zinc oxide is reduced and enters again into the reaction.

Goerlich and Wichmann heat together in an autoclave provided with a stirring gear, a mixture of sodium nitrite, carbon disulphide, and hydrogen sulphide for the production of thiocyanate. The temperature is maintained at 150° C. and the operation continued until the manometer indicates a lowering of the pressure and therefore the end of the reaction.

According to Raschen and Brock, desulphurization of thiocyanate may be effected by treating it with nitric acid with exclusion of air. If sodium thiocyanate for instance is allowed to flow into dilute nitric acid, hydrocyanic acid and nitric oxide are liberated. The gases are passed through a scrubber with water at 80° C. to retain the nitrous vapors and the hydrocyanic acid passing along is collected in cold water or an alkaline solution. Nitric acid is regenerated from the oxide for reuse.

Lutke secures desulphurization of the thiocyanates by mixing ninety-seven parts of the potassium compound with sixty-five parts of zinc dust and heating the mass in an iron crucible with stirring. When the mass glows the external heat is withdrawn and the reaction allowed to progress. The reaction applied in this way is stated to furnish ninety per cent. of the theoretical yield.

Bower first converts the soluble thiocyanate into the copper salt by double decomposition with cuprous chloride. The copper compound is suspended in an autoclave with finely divided

iron and heated under pressure. Copper sulphide and ferrous cyanide result and the latter is treated with an alkali to produce soluble ferrocyanide.

Tschermiak mixes thiocyanate with ninety per cent. of its weight of dried oxide of iron and heats the mixture at 450° C. for one hour. The resulting mass contains an amount of cyanate corresponding with 90 per cent. of the theoretical yield, together with a little alkaline sulphate. The cyanate is purified by recrystallization at 0° C. when the sulphate separates.

To prevent the production of cyanates in the treatment of ferrocyanide for cyanide, Chaster grinds together the anhydrous ferrocyanide and alkaline carbonate in proper proportions and mixes the mass with finely divided wood-charcoal, or with gas-tar, resin, bitumen or similar substances, after which it may be treated in the furnace in the usual way.

In the reactions and processes here set forth, even though they may not all be operative and though some may even be questionable, there is food for fruitful study and much help for future work. And they illustrate the promptness with which rational investigation responds to the commercial demand.

WM. MCMURTRIE.

OBITUARY.

VICTOR MEYER, who died on the 8th of August, was born in Berlin on the 8th of September, 1848. His first published chemical investigation appeared in April, 1869, and was published from the laboratory of Professor Baeyer, who was at that time professor of chemistry at the Gewerbe Academie in Berlin.

In 1871 Meyer was made professor of chemistry at Stuttgart; in 1872 he was called to Zurich; in 1885 he went as professor of chemistry to the University of Göttingen, where he remained until 1889, when, upon the retirement of Professor Bunsen, Meyer was called to his place as professor of chemistry in the University of Heidelberg.

Meyer was an extremely active and able chemical investigator. His activity is shown by the fact that since the appearance of his first paper in 1869 there have appeared in the *Berichte der deutschen chemischen Gesellschaft*, up to the time of his death, 275 separate papers from his pen, with hosts of other papers from his laboratory, the work of which was suggested and inspired by him. Besides the papers published in the *Berichte*, occasional

papers have appeared in Liebig's *Annalen*, the *Journal für praktische Chemie*, the *Zeitschrift für physikalische Chemie*, and the *Zeitschrift für anorganische Chemie;* added to these are lectures and addresses published in the more popular journals. While the large number of his published papers testifies to his activity, their intrinsic worth and the unusual number of really important papers among them gives ample evidence of his great ability.

One of his early investigations gave to organic chemistry the reaction

$$C_6H_5SO_3K + HCOONa = C_6H_5COONa + KHSO_3,$$

which is now frequently made use of to introduce the carboxyl group into aromatic compounds. Meyer was the first to prepare a nitro-paraffin, and practically all that is known about this interesting group of compounds is due to Meyer and his pupils. His work upon the ammonium bases and his discussion with Ladenberg over the points raised, a discussion which unfortunately mingled with considerable personal feeling on the part of these two experimenters, is familiar to most students of organic chemistry.

In 1883 Meyer announced his discovery of thiophene in commercial coal-tar benzene, which in spite of its large contents of sulphur, had been previously overlooked on account of the close resemblance of its properties to the properties of benzene. Following this came a long series of articles by Meyer and his pupils, giving full accounts of thiophene and its derivatives.

In 1882 Meyer and Janny made clear the structure of the oximes, and in the following year Meyer and Goldschmidt, in studying the action of hydroxylamines on benzil, obtained two isomeric benzil dioximes. A careful study of these compounds forced them to the conclusion that they both had the same structural formula. In 1888 Meyer and Auwers attempted to explain this isomerism by considerations based upon the stereochemistry of carbon. Van't Hoff and Wislicenus have assumed that when carbon atoms are singly linked there is free rotation around their common axis. They pointed out that unless this free rotation was assumed isomeric modifications would result. Meyer and Auwers suggested that the evidence of the two iso-

meric benzil dioximes could be explained if free rotation in their case were not assumed. It is necessary, according to this view, to assume two different kinds of single union between two carbon atoms, one which permits of free rotation, and one which does not.

Later in the same year Meyer and Reicke put forward an ingenious hypothesis concerning the nature of valence in the carbon atom in order to explain the lack of free rotation in some cases of singly linked carbon atoms. These views have never strongly appealed to chemists. One probable reason for this being that the speculations of Meyer and Reicke were followed very closely by a paper from Hantzch and Werner upon the stereochemistry of nitrogen, in which the isomerism of the oximes was referred to the nitrogen atoms in a manner that gave a simpler, and on the whole, more satisfactory explanation of the subject.

Stereochemistry (a name which by the way was first suggested by Meyer), has been a favorite field of investigation for Meyer, and he has made many contributions, both experimental and theoretical, to the rapid advance of this subject.

In 1894 Meyer introduced to the chemical world a new series of organic bases which contained iodine but no nitrogen, which he called iodonium bases.

Meyer's work has not been limited to the field of organic chemistry. His apparatus for the determination of the vapor-density of liquids and solids is perhaps in more common use than any other.

By using platinum and porcelain vessels he has studied the vapor-density of numerous inorganic compounds and elements at a white heat. In this connection I cannot do better than quote from an address made by Meyer, at Heidelberg, in 1889: "To-day new methods of experiment permit of comparatively easy determination of the vapor-density and consequently of the molecular state of substance at the highest temperatures. Numerous inorganic compounds, and the elements themselves, have been studied with regard to their vapor density at a white heat. While many of them, as oxygen, nitrogen, sulphur, and mercury, remain unchanged under such conditions, the molecules

of chlorine, bromine, and iodine were split into two atoms in conformity with Avogadro's surmise in regard to the compound nature of the elementary molecules. In the same manner the vapor-density and the molecular condition of the less volatile elements, zinc, thallium, antimony, and bismuth were successfully determined at a white heat. To-day pyrochemical work is limited to a temperature of 1,700° C., because vessels of porcelain and platinum, to the use of which we are limited, fuse above that temperature.

"The possibility of performing quantitative experiments at those temperatures seemed to us, some few years ago, to be an unexpected progress, but to-day we complain that the trivial cause of a want of proper vessels forbids us to increase the temperature to 2,000° or 3,000° C. There is no doubt that we should arrive at new unthought-of facts, that the splitting of other elementary molecules would be possible, that a new chemistry would be revealed to us, if, being provided with vessels of infusible material, we could work at temperatures at which water could not exist, and at which detonating gas would be a non-inflammable mixture."

In 1885 Meyer published a monograph upon his pyrochemical investigations. In 1888 he published another monograph upon thiophene and its derivatives. At the time of his death he was engaged with his colleague, Professor Paul Jacobson, in the preparation of a manual of organic chemistry, the second volume of which approaches completion. This work, so far as published, is the best extended treatment of the subject known to the writer.

The death of Victor Meyer in the midst of his work and in the prime of life is an irreparable loss to chemistry—it is a loss that will be much lamented wherever chemistry is studied.

G. M. RICHARDSON.

SEPTEMBER 21, 1897.

BOOKS RECEIVED.

Electric Smelting and Refining. The Extraction and Treatment of Metals by Means of the Electric Current. Being the second edition of "Elektro-Metallurgie." By Dr. W. Borchers. Translated, with additions, by Walter G. McMillan. London: Charles Griffin & Co., Limited;

Philadelphia: J. B. Lippincott Company. 1897. xx + 416 pp. Price, $6.50.

Cider Vinegar of Pennsylvania. By Dr. William Frear. Bulletin No. 22, Pennsylvania Department of Agriculture. Harrisburg, Pa. 27 pp.

Verzeichniss sämmtlicher Präparate, Drogen und Mineralein mit Erlänterungen. E. Merck, Darmstadt. 1897. vi + 306 pp.

Soil Moisture: A Record of the Amount of Water contained in Soils during the Crop Season of 1896. By Milton Whitney and Ralph S. Hosmer, U. S. Department of Agriculture, Division of Soils. Washington: Government Printing Office. 1897. 23 pp.

Monthly List of Publications of the U. S. Department of Agriculture, Division of Publications. Washington, D. C. September, 1897. 3 pp.

An Introductory Course in Quantitative Chemical Analysis. By Percy Norton Evans, Ph.D., Associate Professor of Chemistry in Purdue University, Lafayette, Indiana. Boston: Ginn & Company. 1897. pp. iv + 83. Price, 55 cents.

The Principles of Chemistry. By D. Mendeléeff. Translated from the Russian (Sixth Edition) by George Kamensky, A. R. S. M. Edited by T. A. Lawson, B.Sc., Ph.D. Vol. I. xviii + 621 pp. Vol. II. i + 518 pp. 1897. New York: Longmans, Green & Co. Price, 2 vols., $10.00.

Manual of Qualitative Chemical Analysis. By the late Dr. C. Remigius Fresenius. Authorized translation by Horace L. Wells, M.A. New Edition, Thoroughly Revised, from the Sixteenth German Edition. xvii + 748 pp. 1897. New York: John Wiley & Sons. Price, $5.00.